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THE NUCLEI OF ATOMS AND THE NEW PERIODIC SYSTEM.

By W. D. Harkins.

Synopsis.

Structure of atomic nuclei; helium-hydrogen hypothesis. The present paper is a summary and extension of previous articles by the author on this subject. Besides the direct evidence afforded by radioactive transformation and by the disruption of atomic nuclei by alpha rays, the data upon which any theory of nuclear structure must be based are atomic masses, atomic numbers which are supposed equal to nuclear charges, and atomic stabilities which are supposed to be related to the relative abundance of the elements in nature. Now the fact that the atomic weights of the 27 lightest elements and of the radioactive elements are approximately integers and that the difference in atomic weight between elements whose atomic numbers differ by a multiple of 2 is usually a multiple of 4, suggests that the nuclei of these elements are built up of hydrogen and helium nuclei. *Assuming* (1) that the nuclei consist only of helium nuclei (α), hydrogen nuclei (η) and electrons (β); (2) that the mass of a nucleus is very nearly equal to the sum of the masses of its constituents; and (3) that the number of hydrogen nuclei, except as combined to form helium nuclei, is never more than 3 (except when the the mu (μ) group ($\eta_2\beta_2$) characteristic of isotopes is also present), the *formulae for the composition of each of the nuclei of the first 27 elements and of the radioactive elements* may be determined from the atomic weights and the atomic numbers. These formulae are given in Tables II. and III. Remarkable regularities are found. With the exception of beryllium ($\alpha_2\eta\beta$), all the atomic nuclei of the *even-numbered light elements* seem to consist merely of helium nuclei, with a pair of cementing electrons added in the case of the higher numbers; while the *odd numbered light elements*, except nitrogen ($\alpha_3\eta_2\beta$) and scandium ($\alpha_{11}\beta$ or more probably $\alpha_{11}\eta\beta_2$) differ from even elements only by each containing an additional group ($\eta_2\beta_2$). The fact that the odd elements are much less abundant in nature than corresponding even elements suggests that odd light elements are less stable, due presumably to the added group $\eta_2\beta_2$. If this group exists as a separate atom, it is an isotope of hydrogen with an atomic weight 3 and may be the hypothetical *nebulium*. It is suggested that this group $\eta_2\beta_2$ and the helium nucleus, assumed to have the composition $\eta_4\beta_2$, each consist of two ring- or disk-shaped electrons with respectively three and four hydrogen nuclei arranged symmetrically between them. The *stability* of various atomic structures is discussed on the basis of the formulae. It is pointed out that *binding and cementing electrons* usually occur in pairs; there are, however, several exceptions. As for the *radioactive elements*, the corresponding elements of the thorium and uranium series differ in weight by 2 units and their formulae are alike except

for the presence of the additional group $\eta_2\beta_2$ or μ group in each element of the uranium series. The latest determinations of the atomic weights of these elements indicate that they are all approximately integers and that the loss of mass due to packing in the nuclei is very small. Why the *elements with numbers from 28 to 80* do not fall in with this scheme can be explained only by assuming that in most cases they consist of mixtures of isotopes. Chlorine, silicon, magnesium, and neon, among the light elements are also mixtures of isotopes. The conclusion from all of the above is that the hydrogen nucleus is the positive electron. In a note appended at the time of correcting the proof for this paper, the writer states that his latest atomic weight results seem to indicate that he has obtained *an experimental separation of chlorine into isotopes. This is the first separation of an element into atomic species which has ever been obtained experimentally.*

ALL of the available evidence indicates that the structure of the nucleus of an atom is not only independent of, but is also much more complicated than that of the outer planetary system of electrons. This is in accord with the theory of Rutherford, which indicates that the nucleus is very minute in comparison with the atom as a whole, and has a diameter of the order of 10^{-13} cm. The number of atoms already discovered, whose nuclei have different structures, amounts to approximately 119, while the number of elements whose non-nuclear planetary systems differ in arrangement is at present only 86, which suggests that the nuclear structure is the less simple. It is also very much more difficult to secure evidence in regard to nuclear structure than with respect to the arrangement of the outer electrons, since the latter manifests itself in almost all of the chemical and physical properties of materials, while with the exception of mass properties, none of the characteristics of the nucleus give indications which are at present observable, except at the time of its disintegration during what is called a radioactive change.

The only ordinary physical property which is now known to be dependent on the nature of the nucleus, aside from those due to its net positive charge, and the minute differences in the wave-lengths in the spectra of isotopes, is that of mass. The ordinary or Mendeléef periodic system of the elements, is an expression of the arrangement in space of the planetary electrons,[1] and is not directly related in its periodicity to any of the following properties which are often discussed as depending upon it: mass, atomic stability, disintegration, and evolution, and the relative abundance of the different atomic species. That there is a second periodic system related to these properties was discovered by me in 1915. The new system is distinguished from that of Mendeléef in a number of ways. First, it is not based on the element numbers, or the so-called atomic numbers, but upon the number of the atomic species.

[1] See references at the end of the paper.

It is somewhat unfortunate that the element numbers of Rydberg, van den Broek, and Moseley, have commonly been styled atomic numbers, since this term should have been reserved for the number of the atomic species. Second, while in the ordinary periodic system the periods are 2, 8, 18, and 32 elements in length, in the new system 2 atomic species are sufficient to constitute a complete period. Third, the new system, as has already been stated, relates to an entirely distinct set of properties.

THE STRUCTURE AND COMPOSITION OF THE NUCLEI OF ATOMS.

In 1915 the writer published formulæ for the composition of atoms, and these give the following system of composition for the nuclei of the atoms carbon, nitrogen, and oxygen:

$$\begin{aligned} \text{Carbon nucleus} &= \alpha_3{}^{++} \\ \text{Nitrogen nucleus} &= \alpha_3{}^{++}h_2\beta^- \\ \text{Oxygen nucleus} &= \alpha_4{}^{++} \end{aligned}$$

where α^{++} is used as the symbol for the nucleus of the helium atom or the alpha particle, h^+ indicates the nucleus of the hydrogen atom, and β^- stands for the negative electron. A considerable amount of evidence in favor of this hydrogen-helium structure of the atoms was presented in this series of papers, which has now received still further confirmation in the driving out of h^+ or $h_2\beta^+$ particles from the nuclei of nitrogen atoms in the experiments of Sir Ernest Rutherford.[1]

The object of the present paper is to give further details of this hydrogen-helium theory of atomic structure, and these details will be summarized in a series of postulates. While these postulates have not been presented before in their present form, the evidence bearing upon them has been presented in part in the earlier papers of this series, and will not be repeated here, even though its omission will cause the assumptions to seem much more arbitrary than is actually the case. For such evidence the earlier papers should be consulted.[1] The postulates will be divided as closely as seems justified into three general classes: first, those of a general nature concerning charge and mass; second, those which relate to the presence of helium nuclei in the nuclei of other atoms, and third, those which consider the inclusion of hydrogen nuclei.

[1] Phil. Mag., *37*, 537–87, (1919). It is of interest to note that if in these experiments the α_3 group remains intact and $h_2{}^+\beta^-$ is driven off, then the atom which would be formed is carbon, if $h^+\beta^-$ is driven out, the remaining nucleus is that of an isotope of nitrogen of atomic weight 13, while if h^+ alone is expelled, the remaining nucleus would be that of an isotope of carbon of atomic weight 13.

GENERAL ASSUMPTIONS CONCERNING CHARGE AND MASS.

Postulate 1.—The positive charge on the nucleus of an atom is equal in magnitude to the sum of the negative charges on all of the non-nuclear or planetary electrons. The positive charge on the hydrogen nucleus is equal in this sense to that of one negative electron. This postulate is present in almost all theories of atomic structure.

Postulate 2.—The mass of a complex atom is nearly equal to the sum of the masses of the atoms from which it is built. The evidence for this postulate has been given in the first two papers of this series, and shows that there is very little change of mass when alpha particles unite to form a complex atom with an atomic weight of 56 or less. Calculations made on the basis of the theory of relativity indicate that the loss of mass during the change of uranium into lead (radium G) is equal to only 0.052 of a unit of atomic weight, even although 8 alpha and 6 beta particles are emitted in the change. There is thus very little "packing effect" during alpha disintegrations or aggregations. If the helium nucleus is built up from four hydrogen nuclei, or the helium atom from four hydrogen atoms, then the loss of mass in this process is 0.77 per cent. This is a much more mild assumption than that of Nicholson, according to whom the helium nucleus is built up from two hydrogen nuclei, which unite, occupying the same space, and thus undergo an increase of mass amounting to nearly 100 per cent.

THE HELIUM SYSTEM OF NUCLEAR STRUCTURE.

Postulate 3.—The nuclei of the atoms of even atomic number between numbers 2 and 26 are in general intra-nuclear compounds of alpha particles alone, or of alpha particles and negative electrons.

Postulate 4.—The nuclei of the atoms of even element number between numbers 82 and 92 inclusive, are compounds of the formula $\alpha_m e_n$ for all atoms which are disintegration products derived from thorium, while the members of the uranium disintegration series are intra-nuclear compounds of alpha particles, negative electrons, and hydrogen nuclei, with the general formula $\alpha_m e_n h_2$. Thus the members of the thorium series have the same general formula as the lighter atoms, and may therefore be considered as a continuation of the ordinary system of atoms. The meta-neon supposed to have been found by Thomson and Aston would be a member of the uranium system with a nuclear formula $\eta_4\mu$.

Postulate 5.—As few as three and as many as ten alpha particles may unite to form a stable nucleus without the inclusion of any additional negative electrons or hydrogen nuclei. In atoms thus made up the positive charge on the nucleus is equal to the sum of the positive charges

on the alpha particles, or is $2m$, where m is the number of helium nuclei present. Whenever more than ten alpha particles are present in a compound nucleus, at least two negative cementing electrons are also included, provided the atom is of even atomic number. It is these cementing electrons which are ejected in the beta disintegrations of the radioactive atoms. That the negative cementing electrons are associated in pairs is indicated by the fact that whenever beta disintegrations occur they follow the rule that *there are always two successive disintegrations of this type, or else there is one beta disintegration just preceding and one just after an alpha disintegration*, while in three cases as many as four or five alpha disintegrations occur in direct succession.

The atomic weights and nuclear charges of the atoms taken together indicate that just as the nucleus of a radioactive atom may lose as many as five alpha particles in direct succession, so as many as 8 alpha particles, each carrying two positive charges and with a mass of four, may unite to form a sulphur atom nucleus with a positive charge of 16 and a mass of 32, and without a single cementing electron; but the nucleus of a positive charge equal to 18 and a mass of 36, built from 9 alpha particles alone seems not to be stable, so the argon nucleus is stabilized by 2 negative electrons, which make it necessary to include one additional alpha particle in order to give the nucleus its proper charge. This gives to the argon atom a mass of 40 instead of the normal 36. On the other hand, a nucleus consisting of ten alpha particles alone, as in the calcium atom, seems to be stable, giving a nucleus of mass 40 and charge 20. However, when the nuclear charge rises to 22 or more, cementing electrons are always included. Thus the titanium nucleus has the formula $(\alpha_{12}e_2)^{22+}$, where the $22+$ indicates the net charge on the nucleus. The number of cementing electrons remains constant at 2 until the nuclear charge rises to 32 in the element germanium, when the number increases to 4.

Whenever an atom has a higher atomic weight than the atom of next higher atomic number, this is due to the fact that the first atom of the pair contains more cementing electrons in its nucleus than the number corresponding to its position with reference to the adjacent elements, or else the second of the pair contains less of such electrons than corresponds with its position.

If the nucleus of the thorium atom is built of alpha particles and cementing electrons alone, as suggested in the preceding section, then it would consist of 58 alpha particles and 26 binding electrons, which would allow 13 pairs of beta disintegrations and 58 alpha ejections in the process of total disruption, while there are 2 pairs of beta changes

and 6 alpha changes in the system from thorium to thorium *E*, the complete disintegration series as now known. The ratio of 2 to 6 is about one and a half times that of 13 to 58, but the former includes both ends of a disintegration series, with beta changes at both of the ends. Also according to the system proposed, cementing electrons add very slowly with increase of atomic number among the light atoms. In the uranium series there are 8 alpha and 3 pairs of beta disintegrations, as compared with 59 of the former and 13 pairs of the latter for total disruption, or the numerical relations are similar to those found in the thorium series. The uranium nucleus, though it is even in number, evidently contains two hydrogen nuclei, and these are present in all of the forms of lead produced by radioactive disintegration from uranium, and in all of the other members of the radium and actinium series. This gives an explanation of the fact that while the difference in atomic weight of isotopes which come from one ancestor, is four, the difference between adjacent isotopes, which descend from different ancestors, is half of four, or two.

In the Harkins-Wilson equation for atomic weights[1]

$$W = 2(N + n) + 1/2 + 1/2(-1)^{N-1},$$

where N is the atomic number, and W the atomic weight, n may be considered as the number of cementing electrons used in attaching helium nuclei. It does not take account of any electrons used in cementing on hydrogen nuclei. For elements of even atomic number this becomes much simpler, or

$$W = 2(N + n). \tag{2}$$

Durrant made a study of this equation[2] and found that n is zero from elements 1 to 17, two for element 18, zero for element 20, and 2 for elements 2 to 28. Beginning with element 29 the value of n begins to increase at an almost constant rate in such a way that the tangent of the angle made by the n line and the atomic number (N) axis, is 1/3.

Equation 2 may be put in the form

$$W = 4\left(\frac{N + n}{2}\right), \tag{3}$$

where the symbols have the same meaning as before, and $(N + n)/2$ is the number of alpha particles in the nucleus of the atom. A simple equation based on these relations is:

$$W = 2\left(N + \frac{N - 26}{2.7}\right) \tag{4}$$

[1] J. Am. Chem. Soc., 37, 1380 (1915).
[2] J. Am. Chem. Soc., 37, 621–7 (1917).

or

$$W = 4\left(\frac{N}{2} + \frac{N - 26}{5.4}\right), \quad (5)$$

where $(N - 26)/5.4$ represents approximately the number of pairs of cementing electrons, or $(N - 26)/2.7$ the number of such electrons. This term is obviously not to be used when it is negative.

One of the characteristics of the radioactive elements is that the increase in the number of cementing electrons with the atomic number is considerably greater than in the case of any other set of elements in the system. Thus the average for elements of high atomic number is the addition of one cementing electron for each increment of 2.7 in the atomic number, while in the radium series between radium-G and uranium, one such electron is added on the average for each increase of 1.66 in the atomic number.

Postulate 6.—While for atoms of even atomic number between 4 and 26 the atomic weights are divisible by 4, and between numbers 82 and 92, each alpha disintegrative change is such as to involve a loss of mass equal to 4; between atomic numbers 30 and 90 this is not true. This is illustrated by Table I., which shows that the rule postulating divisibility by 4 ceases to hold with extreme abruptness at element 28, which is nickel. The simplest assumption is that already made by the writer, and by Durrant, on the basis of the equation proposed by the writer *that the deviation is caused by the existence of isotopes in elements of atomic number higher than 27.* The evidence in favor of this postulate is less than for any of the others. Experimental work on the

TABLE I.

Illustrates the Helium Structure of the Nuclei of Atoms.

Atomic Number.	Atomic Weight Divided by 4.	Deviation from a Whole Number.
2	1.00	0.00
6	3.00	0.00
8	4.00	0.00
10	5.00	0.00
12	6.08	+0.08
14	7.07	+0.07
16	8.01_8	$+0.01_8$
18	9.97	−0.03
20	10.02	+0.02
22	12.02_8	$+0.02_8$
24	13.00	+0.00
26	13.96	−0.04

Average deviation from a whole number up to this point is the extremely small amount of 0.023.

TABLE I.—*Continued.*

28	14.50	+0.50
30	16.34	+0.34
32	18.12_5	$+0.12_5$
34	19.80	−0.20
36	20.73	−0.27
38	21.91	−0.09
40	22.65	−0.35
42	24.00	0.00
44	25.42_5	$+0.42_5$
46	26.67_5	-0.32_5

Average deviation from a whole number for 10 elements beginning with element 28 is equal to 0.262, or almost what it should be by chance (0.250). *Notice that the break occurs exactly at element 28 (Ni), which is exactly the same element at which the atomic weights themselves cease to be close to whole numbers.*

diffusion of ordinary elements has been carried on in this laboratory for four years, and a conclusion would probably have been reached in at least one instance if the work had not been interrupted by the war.

THE HELIUM-HYDROGEN SYSTEM OF NUCLEAR STRUCTURE.

Postulate 7.—While among the lighter atoms the atoms with an even nuclear charge are in general intra-atomic compounds of helium alone, and the nuclei are intra-nuclear compounds of alpha particles alone, or of alpha particles plus cementing negative electrons, the nuclei which carry an odd numbered positive charge have the same composition as the nucleus of next lower even charge with the addition of r hydrogen nuclei and $r - 1$ negative electrons. The value of r is almost always 3, but in the exceptional case of nitrogen it is 2.

Postulate 8.—The helium nucleus consists of 4 hydrogen nuclei and 2 negative electrons, which serve to bind the hydrogen nuclei together. This postulate has also been assumed by Rutherford.

Postulate 9.—In the helium nucleus the hydrogen nuclei or positive electrons are bound to the negative electrons, but not to each other. That this is the case is indicated by the sign of the mutual electromagnetic mass or the "packing effect" which amounts to a loss of mass of 0.77 per cent. The loss of mass shows that the particles which have come together attract each other, and that the distance of approach is such that the centers of positive and negative electrons are distant about 400 times the diameter of the positive electron. If the positive electron is as small as is assumed by Rutherford, this would mean that the positive electron would lie very near the outer part of the negative electron; and that the alpha particle is probably not much larger than two negative electrons.

TABLE Ib.

Deviations of the Ttomic Weights from Whole Numbers, Showing that for the Heavier Elements there is no Tendency for these Weights to Approximate Whole Numbers, while the Atomic Weights of the Elements below No. 28 are Extremely close to Whole Numbers.

Lighter Elements Without Isotopes.[1]				Heavier Elements Which Contain Isotopes.										
At. No.	Element.	At. Wt.	Diff. from Whole No.	At. No.	Element.	At. Wt.	Diff. from Whole No.	Probable Error in At. Wt.	At. No.	Element.	At. Wt.	Diff. from Whole No.	Probable Error in At. Wt.
2	He...	4.00	0.00	28	Ni ...	58.68	0.32	0.02	49	In...	114.8	0.2	0.5
3	Li ...	6.94	0.06	29	Cu...	63.57	0.43	0.05	50	Sn...	118.70	0.30	0.2
4	Be...	9.1	0.10	30	Zn...	65.37	0.37	0.05	51	Sb...	120.2	0.2	0.3
5	B....	10.9	0.10	31	Ga...	70.1	0.10	0.5	52	Te...	127.5	0.5	0.2
6	C....	12.0025	0.0025	32	Ge...	72.5	0.50	0.5	53	I....	126.92	0.08	0.03
7	N....	14.008	0.008	33	As ...	74.96	0.04	0.05	54	Xe ..	130.2	0.2	0.2
9	F....	19.005	0.005	34	Se ...	79.2	0.20	0.1	55	Cs...	132.81	0.19	0.05
				35	Br ...	79.923	0.08	0.1	56	Ba ..	137.37	0.37	0.03
Av. variation...			0.039	36	Kr...	82.92	0.08	0.1	57	La...	139.0	0.0	0.3
				37	Rb...	85.45	0.45	0.05	58	Ce ..	140.25	0.25	0.1
11	Na...	23.00	0.00	Av. variation..			0.247		Av. variation..			0.229	
13	Al ...	27.10	0.10										
15	P....	31.02	0.02						73	Ta ..	181.5	0.5	1.0
16	S....	32.07	0.07						74	W...	184.0	0.0	0.5
									76	Os...	190.9	0.1	0.4
Av. variation...			0.047						77	Ir ...	193.1	0.1	0.2
									78	Pt...	195.2	0.2	0.1
				38	Sr ...	87.63	0.37	0.03	79	Au ..	197.2	0.2	0.1
18	Ar ...	39.9	0.10	39	Y....	89.0	0.0	0.2	80	Hg ..	200.6	0.4	0.4
19	K....	39.10	0.10	40	Zr ...	90.6	0.4	0.2					
20	Ca...	40.07	0.07	41	Cb...	93.5	0.5	...	Av. variation..			0.214	
22	Ti ...	48.10	0.10	42	Mo ..	96.0	0.0	0.1					
23	V....	51.00	0.00	44	Ru...	101.7	0.3	0.1	81	Tl...	204.0	0.0	0.2
24	Cr ...	52.00	0.00	45	Rh...	102.9	0.1	0.05	82	Pb ..	207.20	0.20	0.1
25	Mn ..	54.93	0.07	46	Pd...	106.7	0.3	0.1	88	Ra ..	226.0	0.0	0.1
26	Fe ...	55.84	0.16	47	Ag...	107.88	0.12	0.02	90	Th ..	232.15	0.15	0.1
27	Co...	58.97	0.03	48	Cd...	112.4	0.4	0.03	92	U ...	238.16	0.16	0.1
Av. variation...			0.070	Av. variation..			0.247		Av. variation..			0.102	

Note. One of the remarkable features of this table is that the average deviation from a whole number is very low for both the light and the heaviest atoms, but is large between atomic numbers 28 and 80.

[1] A complete table of the lighter elements will be found in the Journal of the American Chemical Society, *37*, 1370 (1915). The above table gives the elements just before and just after element 28 (Ni) to show the break at that point. The elements Ne, Mg, Si, and Cl, have been omitted from the list of the lighter atoms because each of them is a mixture of two isotopes. It will be seen that where isotopes do not exist the atomic weights are very close to whole numbers.

Postulate 10.—This postulate is more definite than our present evidence, but seems to be better in accord with available knowledge than any other assumption which has occurred to the writer. The helium nucleus is assumed to consist of two negative electrons which have the form of rings, or discs, or spheres flattened into ellipsoids. The rings or discs lie with their greatest dimension perpendicular to the axis of the nucleus, and far from each other relative to their dimensions, between the two discs near their edges are the positive electrons in a symmetrical arrangement, that is at the corners of a square (Fig. 1).

Postulate 11.—Since a nucleus built according to the model assumed in

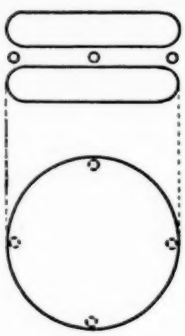

Fig. 1.

Model representing the relative position but not the shape, of the positive and negative electrons in the helium nucleus. The two large discs represent negative electrons and the four small circles represent hydrogen nuclei.

postulate 10 would be electrically negative on the outside, it may be assumed to be incapable of closely binding any negative electrons alone. Also, since its net positive charge is equal to two, it may also be assumed that it will not bind with itself any positive electrons unless it at the same time adds on at least one negative electron. However, such nuclei may unit with each other, since each is at the same time positive and negative.

Postulate 12.—However, two helium nuclei alone do not make a stable structure except when one positive and one negative electron are included (nucleus of beryllium or glucinium), but from three to nine helium nuclei may unite together without any other binding particles. This seems to indicate a tube, ring, or a shell structure for the nuclei of complex atoms, although the ring or shell is probably very closely packed.

Postulate 13.—The group consisting of three hydrogen nuclei and two negative electrons is contained in the nucleus of every atom of odd atomic number between 3 and 27 inclusive, except only nitrogen and scandium. This group is very similar in composition to the helium nucleus, since it contains the same number of negative electrons and only one less positive electron.

Postulate 14.—The extremely frequent occurrence of the group h_3e_2 suggests that it probably occurs alone as a unit.[1] In this case it would be the nucleus of an atom of a nuclear charge equal to one, and in this sense would be an isotope of hydrogen. However, since the frontier of such an atom is much less extensive and much nearer the nucleus than in the radioactive atoms, the atom might not be isotopic with hydrogen in the sense of its spectrum or chemical behavior, although it would probably be very similar. If the hypothetical nebulium exists at all, it is probably this form of hydrogen. One of the arguments in favor of the existence of nebulium is that Fabry and Buisson[2] found by a study of the Döppler effect that its atomic weight is close to 2.7, which, since the method is not exact, was interpreted as an indication that its atomic weight is 3. It is easily seen that the isotope of hydrogen would give just this atomic weight. It is possible that some of this isotope is present in ordinary hydrogen, but since it would probably be an extremely small fraction of the hydrogen, it is likely that its separation would be difficult or impossible. A model for this eka-hydrogen nucleus might well take just the form of that for the helium nucleus, with the substitution of three positive hydrogen nuclei at the corners triangle for the four hydrogen nuclei of the alpha particle.

Postulate 15.—Since the elements whose atomic nuclei carry an odd numbered charge are very much less abundant than those for which the charge is even, and since the former alone contain the eka-hydrogen nucleus, it is evident either that nuclei built of helium nuclei alone are very much the more stable, or else the supply of eka-hydrogen was not very great when such atoms were built.

Postulate 16.—There is a little evidence which seems to suggest that the nuclei of odd-numbered charge are formed from those which have an even charge. This would indicate that in the primary formation of atomic nuclei the aggregation of alpha particles is the primary reaction, and that the eka-hydrogen nuclei $(h_3e_2)^+$ or the h_2e group adds on later. The evidence which points in this direction is that obtained in the new periodic system discovered by the writer as given in Fig. 2, which gives the percentage abundance of the elements in the meteorites as ordinates and the atomic numbers as abscissæ. It may be noted that every even-numbered element is very much more abundant than the adjacent element of odd atomic number, but what is specially in point here is that every one of the more abundant elements of odd number, sodium, aluminium, cobalt, phosphorus, and potassium, lies adjacent to a high

[1] This group will be called a nu (ν) particle.

[2] Astrophys. J., *40*, 256 (1914).

peak for an even number. This is, of course, not at all conclusive, especialy since fluorine, which lies next to oxygen, is not very abundant, but it seems to be in accord with the relations found by Rutherford in the breaking down of the nitrogen nucleus. At least he comes to the conclusion that the hydrogen nuclei are about twice the diameter of the electron away from the center of the complex nucleus,[1] or 7×10^{-13} cm. distant, which is probably near the outer part of the nucleus, and that

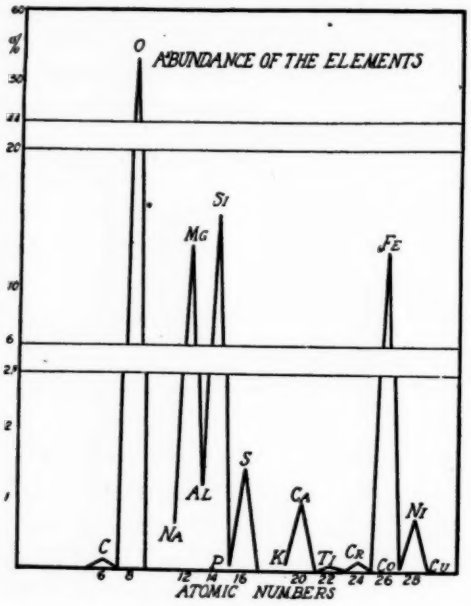

Fig. 2.

Atomic percentage abundance of the atoms in 350 stone to 10 iron meleorites, which is in the ratio of known falls. This is supposed to represent the average composition of materials as perfectly as can now be determined.

at least one of these hydrogen nuclei is driven off in a collision with a fast alpha particle.

Postulate 15 is taken from the earlier papers of the writer,[2] which indicate that of all complex nuclei that of helium and probably also that of the hypothetical meta-hydrogen, that is the nu particle, are by far the most stable, indeed the stability of the α particle is of an entirely higher order than that of other nuclei. Next in order of stability come the nuclei of the light atoms of even atomic number or nuclear charge, that is the nuclei consisting of alpha particles alone, or of alpha particles a pair of and negative electrons. The least stability is that concerned

[1] Phil. Mag., *37*, 586 (1919).

[2] J. Am. Chem. Soc., *37*, 1393 (1915); *39*, 856–79 (1919).

with cementing on two or even three hydrogen nuclei in the groups $h_2\beta$ or $h_3\beta_2$. These groups do not seem to be present in the radioactive nuclei of the heavy atoms. It is to be noted that these theoretical findings have been confirmed by Rutherford's discovery.

Postulate 17.—The presence of an odd number of negative electrons in a nucleus leads to instability, and a low abundance of the atoms, whenever the nucleus consists of alpha particles and negative electrons alone. This relation is found to hold among the radioactive atoms, whether mu (μ) particles are present or absent ($\mu = h_2\beta_2$).

COMPOSITION OF THE NUCLEI OF ATOMS.

The composition of the nuclei of the atoms of low atomic number is given in Table II., while that for the atoms of high atomic number is presented in Table III.

TABLE II.

Composition of Light Atoms and Their Nuclei.

Atoms of Even Nuclear Charge.					Atoms of Odd Nuclear Charge.				
Symbol.	Formula of		Non-nuclear Electrons.		Symbol.	Formula of		Non-nuclear Electrons.	
	Atom.	Nucleus.	Inner.	Valence.		Atom.	Nucleus.	Inner.	Valence.
He.....	He	α	e_2	..	[Li.....	HeH_3	$\alpha\nu$	e_2	e
Be.....	He_2H	$\alpha_2(\eta\beta)$	e_2	e_2	B.....	He_2H_3	$\alpha_2\nu$	e_2	e_3
C.....	He_3	α_3	e_2	e_4	N.....	He_3H_2	$\alpha_3(\eta_2\beta)$	e_2	e_5
O.....	He_4	α_4	e_2	e_6	F.....	He_4H_3	$\alpha_4\nu$	e_2	e_7
Ne.....	He_5	α_5	e_{10}	..	Na....	He_5H_3	$\alpha_5\nu$	e_{10}	e_1
Mg....	He_6	α_6	e_{10}	e_2	Al.....	He_6H_3	$\alpha_6\nu$	e_{10}	e_3
Si.....	He_7	α_7	e_{10}	e_4	P.....	He_7H_3	$\alpha_7\nu$	e_{10}	e_5
S.....	He_8	α_8	e_{10}	e_6	*Cl*.....	He_8H_3	$\alpha_8\nu$	e_{10}	e_7
A.....	He_{10}	$\alpha_{10}\beta_2$	e_{18}	..	K.....	He_9H_3	$\alpha_9\nu$	e_{10}	e_1
Ca.....	He_{10}	α_{10}	e_{18}	e_2	Sc.....	$He_{11}H$	$\alpha_{11}\beta\eta_2$	e_{18}	e_3
Ti.....	He_{12}	$\alpha_{12}\beta_2$	e_{18}	e_4	V.....	$He_{12}H_3$	$\alpha_{12}\nu\beta_2$	e_{18}	e_5
Cr.....	He_{13}	$\alpha_{13}\beta_2$	e_{18}	e_6	Mn ...	$He_{13}H_3$	$\alpha_{13}\nu\beta_2$	e_{18}	e_7
Fe.....	He_{14}	$\alpha_{14}\beta_2$	e_{18}	e_8	Co....	$He_{14}H_3$	$\alpha_{14}\nu\beta_2$	e_{18}	e_9

NOTATION.

$\eta = h^+$ = positive nucleus of hydrogen atom, or the positive electron.

$\alpha = he^{++} = \eta_4\beta_4$.

$\nu = \eta_3\beta_2 = h_3{}^+\beta_2$.

β = negative electron in the nucleus, and e = electron in non-nuclear system.

Note.—The symbols in italics represent elements for which it is probable that more than one isotope exists, in which case only the formula for one isotope is given. The bracket incloses ISOMERIC atoms. *Note should be taken of the fact that of the thirteen nuclei of odd charge in only one case is the odd charge due to an odd number of negative electrons, and in twelve cases it is due to an odd number of hydrogen nuclei in the nu (ν) group.* The probable formulae of the isotopic atoms are chlorine $\alpha_8\nu\mu\epsilon'_{10}e_7$, silicon $\alpha_7\mu\epsilon_{10}e_4$, magnesium $\alpha_6\mu\epsilon_{10}e_2$, and neon $\alpha_5\mu\epsilon_{10}$.

TABLE III.

Composition of Heavy Atoms.

A. Uranium Series in order of Disintegration.

Symbol of Element.	Nuclear Charge and No. of External Electrons.	Symbol of Atom.	Formula of		Non-nuclear Electrons.		Type of Change.	Atomic Wt.
			Atom.	Nucleus.	Inner.	Valence.		
U....	92	U	$He_{59}H_2$	$\alpha_{59}\eta_2\beta_{28}$	e_{86}	e_6	α	238
Th...	90	UX_1	$He_{58}H_2$	$\alpha_{58}\eta_2\beta_{28}$	e_{86}	e_4	β	234
Bv...	91	UX_2	$He_{58}H_2$	$\alpha_{58}\eta_2\beta_{27}$	e_{86}	e_5	β	234
U....	92	U_2	$He_{58}H_2$	$\alpha_{58}\eta_2\beta_{26}$	e_{86}	e_6	α	234
Th...	90	Io	$He_{57}H_2$	$\alpha_{57}\eta_2\beta_{26}$	e_{86}	e_4	α	230
Ra...	88	Ra	$He_{56}H_2$	$\alpha_{56}\eta_2\beta_{26}$	e_{86}	e_2	α	226
Nt...	86	Ra Em	$He_{55}H_2$	$\alpha_{55}\eta_2\beta_{26}$	e_{86}	..	α	222
Po...	84	Ra A	$He_{54}H_2$	$\alpha_{54}\eta_2\beta_{26}$	e_{78}	e_6	α	218
Pb...	82	Ra B	$He_{53}H_2$	$\alpha_{53}\eta_2\beta_{26}$	e_{78}	e_4	β	214
Bi....	83	Ra C	$He_{53}H_2$	$\alpha_{53}\eta_2\beta_{25}$	e_{78}	e_5	β	214
Po...	84	Ra C	$He_{53}H_2$	$\alpha_{53}\eta_2\beta_{24}$	e_{78}	e_6	α	214
Pb...	82	Ra D	$He_{52}H_2$	$\alpha_{52}\eta_2\beta_{24}$	e_{78}	e_4	β	210
Bi....	83	Ra E	$He_{52}H_2$	$\alpha_{52}\eta_2\beta_{23}$	e_{78}	e_5	β	210
Po...	84	Ra F	$He_{52}H_2$	$\alpha_{52}\eta_2\beta_{22}$	e_{78}	e_6	α	210
Pb...	82 (end)	Ra G	$He_{51}H_2$	$\alpha_{51}\eta_2\beta_{22}$	e_{78}	e_4	..	206

Secondary Branch of Uranium Series.

Pb...	82	Ra B	$He_{53}H_2$	$\alpha_{53}\eta_2\beta_{26}$	e_{78}	e_4	β	214
Bi	83	Ra C	$He_{53}H_2$	$\alpha_{53}\eta_2\beta_{25}$	e_{78}	e_5	α	214
Tl....	81	$Ra\ C_2$	$He_{52}H_2$	$\alpha_{52}\eta_2\beta_{25}$	e_{78}	e_3	β	210
Pb...	82	End?	$He_{52}H_2$	$\alpha_{52}\eta_2\beta_{24}$	e_{78}	e_4	..	210

The brackets inclose isomeric atoms.

The formulæ for the nuclei of the atoms of the uranium series may be simplified by putting μ in place of $\eta_2\beta_2$, when the formula of the nucleus of uranium becomes $\alpha_{59}\mu\beta_{26}$ while that of thorium is $\alpha_{58}\beta_{26}$.

B. Thorium Series in Order of Disintegration.

Symbol of Element.	Nuclear Charge and No. External Electrons.	Symbol of Atom.	Formula of		Non-nuclear Electrons.		Type of Change.	Atomic Wt.
			Atom.	Nucleus.	Inner.	Valence.		
Th...	90	Th	He_{58}	$\alpha_{58}\beta_{26}$	e_{86}'	e_4	α	232
Ra...	88	Ms Th_1	He_{57}	$\alpha_{57}\beta_{26}$	e_{86}'	e_2	β	228
Ac...	89	Ms Th_2	He_{57}	$\alpha_{57}\beta_{25}$	e_{86}'	e_3	β	228
Th...	90	Ra Th	He_{57}	$\alpha_{57}\beta_{24}$	e_{86}'	e_4	α	228
Ra...	88	Th X	He_{56}	$\alpha_{56}\beta_{24}$	e_{86}'	e_2	α	224
Nt...	86	Th Em	He_{55}	$\alpha_{55}\beta_{24}$	e_{86}'	..	α	220
Po...	84	Th A	He_{54}	$\alpha_{54}\beta_{24}$	e_{78}'	e_6	α	216
Pb...	82	Th B	He_{53}	$\alpha_{53}\beta_{24}$	e_{78}'	e_4	β	212
Bi....	83	Th C	He_{53}	$\alpha_{53}\beta_{23}$	e_{78}'	e_5	β	212
Po...	84	Th C'	He_{53}	$\alpha_{53}\beta_{22}$	e_{78}'	e_6	α	212
Pb...	82	Pb Th	He_{52}	$\alpha_{52}\beta_{22}$	e_{78}'	e_4	..	208

Secondary Branch of Thorium Series.

Pb...	82	Th B	$\{ He_{53}$	$\alpha_{53}\beta_{24}$	e_{78}'	e_4	β	212
Bi....	83	Th C	$\{ He_{53}$	$\alpha_{53}\beta_{23}$	e_{78}'	e_5	α	212
Tl....	81	Th D	$\{ He_{52}$	$\alpha_{52}\beta_{23}$	e_{78}'	e_3	β	208
Pb...	82	End?	$\{ He_{52}$	$\alpha_{52}\beta_{22}$	e_{78}'	e_4	..	208

The brackets inclose isomeric atoms.

The above changes may easily be written in the form of equations, such as:

$$\underset{\text{Th}}{\alpha_{58}\beta_{26}e_{86}'e_4} \rightarrow \alpha^{++} + 2e^- + \underset{\text{Ms Th}_1}{\alpha_{57}\beta_{26}e_{86}'e_2},$$

$$\underset{\text{Ms Th}_1}{\alpha_{57}\beta_{26}e_{86}'e_2} \rightarrow \underset{\text{Ms Th}_2}{\alpha_{57}\beta_{25}e_{86}'e_3},$$

$$\underset{\text{Ms Th}_2}{\alpha_{57}\beta_{25}e_{86}'e_3} \rightarrow \underset{\text{Ra Th}}{\alpha_{57}\beta_{24}e_{86}'e_4}.$$

The above beta changes are given in abbreviated form. The complete reaction is written:

$$\underset{\text{Ms Th}_2}{\alpha_{57}\beta_{25}e_{86}'e_3} + e^- \rightarrow \alpha_{57}\beta_{24}e_{86}'e_4 + \beta^-.$$

Thus in an alpha change the whole atom loses an alpha particle from the nucleus, and two electrons from the valence layer. In a beta change, while the nucleus loses a beta particle, the valence shell picks up an extra electron, so the *final effect*, so far as the formula is concerned, is the same as if a beta particle had moved from the nucleus into the valence layer. The whole change is similar to a molecular rearrangement, and might be classed as an atomic rearrangement, but with the difference that the electron *gained is not the same individual as that which is lost.* A few equations for members of the uranium series are written below as models from which all of the reactions may be written out.

$$\underset{\text{Ra}}{\alpha_{56}\eta_2\beta_{26}e_{86}'e_2} \rightarrow \alpha^{++} + 2e^- + \underset{\text{Ra Em}}{\alpha_{55}\eta_2\beta_{26}e_{86}'},$$

$$\underset{\text{Ra Em}}{\alpha_{55}\eta_2\beta_{26}e_{86}'} \rightarrow \alpha^{++} + 2e^- + \underset{\text{Ra A}}{\alpha_{55}\eta_2\beta_{26}e_{78}'e_6},$$

$$\underset{\text{Ra A}}{\alpha_{54}\eta_2\beta_{26}e_{78}'e_6} \rightarrow \alpha^{++} + 2e^- + \underset{\text{Ra B}}{\alpha_{53}\eta_2\beta_{26}e_{78}'e_4},$$

$$\underset{\text{Ra B}}{\alpha_{53}\eta_2\beta_{26}e_{78}'e_4} \rightarrow \underset{\text{Ra C}}{\alpha_{53}\eta_2\beta_{25}e_{78}'e_5},$$

$$\underset{\text{Ra C}}{\alpha_{53}\eta_2\beta_{25}e_{78}'e_5} \rightarrow \underset{\text{Ra}}{\alpha_{53}\eta_2\beta_{24}e_{78}'e_6}.$$

The complete beta change may be written:

$$\alpha_{53}\eta_2\beta_{25}e_{78}'e_5 + e^- \rightarrow \alpha_{53}\eta_2\beta_{24}e_{78}'e_6 + \beta^-.$$

Figure 3 gives a diagram representing all of the radioactive disintegrations, with the formula of the nuclei of the uranium-radium and the thorium series. It may be noticed that *corresponding members of the two disintegration series have formulæ which are very similar*, indeed they are identical with the exception that each member of the uranium-radium series contains one μ particle which is absent from the thorium member.[1]

TABLE IV.

Formulæ of Corresponding Atoms in the Disintegration Series.

	Thorium Series.	Radium Series.	
(Ra Th)	$\alpha_{57}\beta_{24}e_{86}\,e_4$	$\alpha_{57}\mu\beta_{24}e_{86}\,e_4$	(Io)
(ThX)	$\alpha_{56}\beta_{24}e_{86}\,e_2$	$\alpha_{56}\mu\beta_{24}e_{86}\,e_2$	(Ra)
(Th Em)	$\alpha_{54}\beta_{24}e_{86}$	$\alpha_{54}\mu\beta_{24}e_{86}$	(Ra Em)
(Th A)	$\alpha_{54}\beta_{24}e_{78}'e_6$	$\alpha_{54}\mu\beta_{24}e_{78}'e_6$	(Ra A)
(Th B)	$\alpha_{53}\beta_{24}e_{78}'e_4$	$\alpha_{53}\mu\beta_{24}e_{78}'e_4$	(Ra B)
(Th C)	$\alpha_{53}\beta_{23}e_{78}'e_5$	$\alpha_{53}\mu\beta_{23}e_{78}'e_5$	(Ra C)
(Th C′)	$\alpha_{53}\beta_{22}e_{78}'e_6$	$\alpha_{53}\mu\beta_{22}e_{78}'e_6$	(Ra C′)
(PbTh)	$\alpha_{52}\beta_{22}e_{78}'e_4$	$\alpha_{53}\mu\beta_{22}e_{78}'e_4$	(Ra D)
(Th D)	$\alpha_{52}\beta_{22}e_{78}'e_3$	$\alpha_{52}\mu\beta_{22}e_{78}'e_3$	(Ra C_2)
End$_1$	$\alpha_{52}\beta_{22}e_{78}'e_4$	$\alpha_{52}\mu\beta_{22}e_{78}'e_4$	End$_1$

If the actinium disintegration series is what it is now supposed to be its corresponding members have the same formulæ as those of the radium series minus one alpha particle and two beta particles, though it is still possible that the corresponding atoms in the two series have identical formulæ.

It is also well known that when four or five alpha particles are lost in succession in any of the three series, each successive disintegration becomes more violent, and the same is true of successive beta disintegrations. This suggests that the alpha particles are grouped in aggregates of four or five or more alpha particles together with binding electrons and that the smaller the aggregate becomes the more unstable it gets for changes of the above type.

The great similarity in the three disintegration series suggests that while there are many possible compositions for the nuclei of isotopes there are usually only a few compositions and probably only a few structures which are of the requisite stability. The likeness in the three disintegration series is extremely remarkable.

[1] If this μ particle exists alone it forms the atoms of an element of *zero* atomic number.

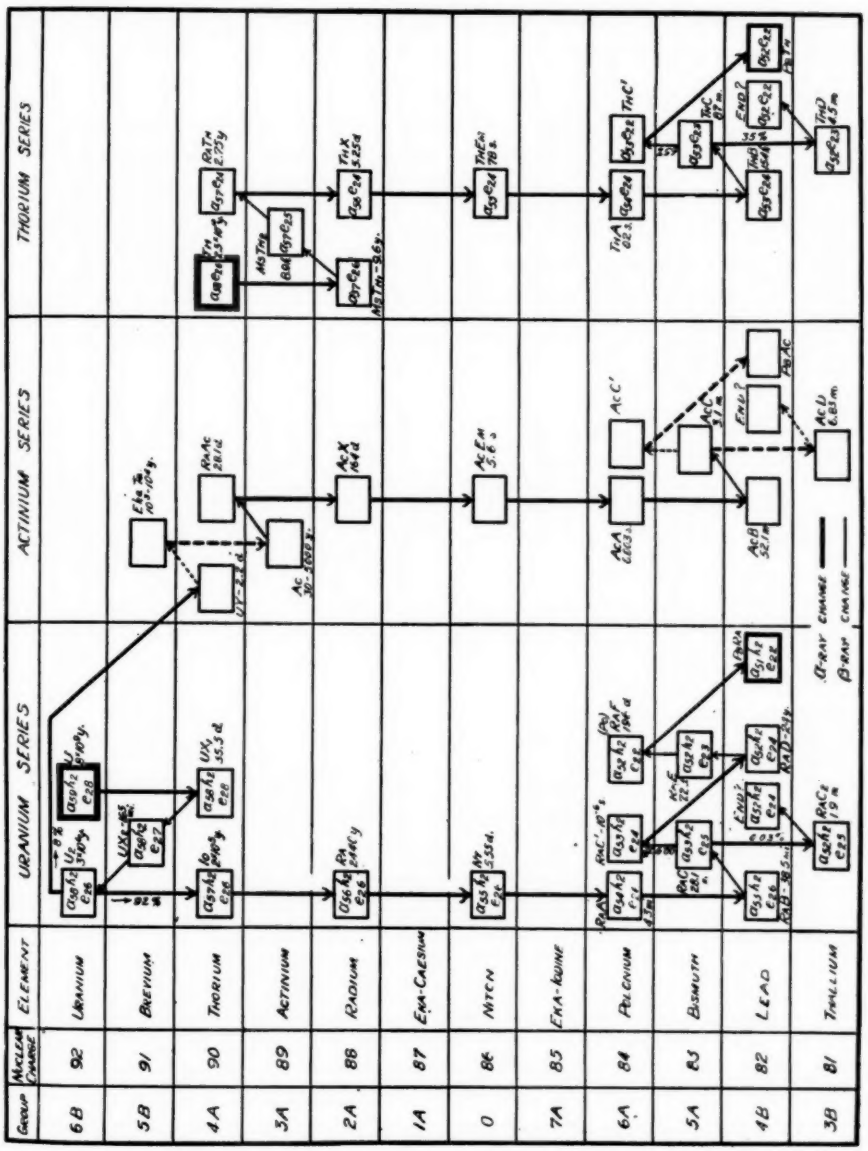

Fig. 3.

Composition of the nuclei of the radio-atoms, with periods of average life. The helium nucleus is represented by α, the hydrogen nucleus by h, and the negative electron by e.

Diagram of the three disintegration series representing the formulæ of the nuclei of atoms. In this diagram the hydrogen nucleus or nu particle, is represented by h, and the negative electron by e. The actinium series may originate in either U_2 as shown in the figure or in U.

ASSOCIATION OF THE NUCLEAR NEGATIVE ELECTRONS IN PAIRS.

Tables II. and III. give an excellent illustration of Postulate 5, that the nuclear negative electrons occur in general in pairs, while there is no such pairing of the alpha particles. Thus among the 26 light atoms there are only 2 (or possibly only one) whose nuclei contain an odd number of electrons, while 24 or 25 contain an even number. Also, among the 30 atomic species of the uranium and thorium series there

are only seven that give formulæ which indicate an odd number of negative electrons in the nucleus. When it is considered that the frequently occurring alpha ($\alpha = h_4e_2$) and nu ($\nu = h_3e_2$) particles, and the μ group of the uranium series which has the formula h_2e_2, all contain two electrons each, the indication of this pairing is very strong. The actinium series in all probability is similar to the ordinary uranium series in this respect.

It will be noticed that the alpha, nu, and mu particles are all held together by two negative electrons each. These may be called *binding* electrons to distinguish them from the *cementing* electrons which hold on the excess alpha particles of the nuclei of the heavier atoms.

Isomeric Atoms, or Atoms of the Same Intra-atomic Formula and Atomic Weight.

Table 3*A* indicates that there are 3 isomeric species of atoms of the formula $He_{58}H_2$, also 3 of the formula $He_{53}H_2$, and 5 with the formula $He_{52}H_2$. In the thorium series there are 3 isomers for each of the formulas He_{57}, He_{53}, and He_{52}. Similar isomers exist in the actinium series. Isomers may be isotopes, as Ra D and the probable end of the secondary uranium series, but usually they are not isotopic. When three isomers occur in succession in a radioactive series, the two latter isomers are formed by two successive beta disintegrations of the nuclei of the respective atoms. In a beta change an electron is lost from the nucleus, and another electron is picked up by the valence shell of electrons by the time the atom has become neutral, so the formula of the complete atom does not change. The nuclei of isomeric atoms are not themselves isomeric unless the atoms themselves are isotopic, but all nuclei of isotopic atoms are not isomeric; so isotopic atoms may be classified as those with isomeric, and those with non-isomeric nuclei. *Of the ordinary atoms calcium and argon are isomeric, the difference in structure being due to the inclusion of two cementing electrons in the argon nucleus, which in calcium are present in the planetary system of non-nuclear electrons.*

Evidence in Favor of Formulæ Proposed for the Heavy Atoms.

While it has been known for some years that the thorium atom loses 6 alpha particles or nuclei of helium atoms during its disintegration, and finally changes into one form of lead, definite formulæ for the atoms of this series have not been assumed previous to this time, for the evidence in regard to the composition of the rest of the nucleus, that contained in this special form of the lead atom, did not seem to be sufficiently com-

plete. Such evidence is to be found in the atomic weights together with the new periodic system discovered by the writer. The detailed study of the atomic weight relations presented in the former papers of this series cannot be summarized here, and should be consulted in the original, but some additional relations will be discussed.

The best determination of the atomic weight of thorium as made by Honigschmid, gave 232.16. This is only 0.16 of a unit more than exactly 58 times the atomic weight given in the atomic weight tables for helium, or 58 times 4.00. The atomic weight of helium is not known to a sufficient degree of accuracy to cause this 0.16 of a unit to receive any consideration, but the atomic weight of oxygen is 4 times 4.000, that of carbon is 3 times 4.001, and that of sulphur is 8 times 4.008. What is more in point is that if we average the atomic weights of the nine elements from 19, potassium, to 27, cobalt, the average deviation of the atomic weight from a whole number is only $-$ 0.012 units. The average has been taken, since it is probable, when the difficulty of obtaining pure samples is taken into account, that this average is more significant than any single determination of the atomic weight. If iron had exactly this average deviation, its atomic weight would be 55.988, or 14 times 3.999, which is exceedingly close to 4.000, while the determined atomic weight of iron is 14 times 3.988. This indicates that when from ten to fourteen helium nuclei form an aggregate, together with one μ particle in 4 of the 9 cases, the atomic weight of the complex atom is almost exactly a whole number times 4.000, or possibly *very* slightly less than this, when alpha particles are present alone, or 3 plus a whole number times 4.00 when nu particles are also present.

Let us consider that the atomic weight given for thorium, 232.12 is exact; this is 58 times 4.002, which is only 0.05 per cent. higher than 4.0000. When the thorium nucleus disintegrates to form its end product in lead it gives off 6 alpha particles, and 4 electrons, so the loss of atomic weight may be assumed to be 6 times 4.00, or 24.00. However, during this disintegration heat to the amount of about 12.9×10^{11} calories are liberated, and when calculated into terms of mass using the relativity method of Einstein, this gives 0.06 grams or 0.06 units of atomic weight, so that 0.06 of the excess 0.12 units of atomic weight have already been accounted for by this short disintegration period. The atomic weight of this isotope of lead is therefore 208.06, which is 52 times 4.0012. When it is considered that these calculations do not involve the atomic weight of helium itself, but its weight in the complex atoms which it forms, it is seen that the agreement is closer than could be expected from numbers determined by experimental work on atomic weights. It might be

better to calculate on the basis of the atomic weights of only those atoms which seem to be aggregates of helium alone. If this is done, using the heavier atoms just preceding those which appear to occur in isotopic forms, that is using calcium, scandium, titanium, chromium and iron, the average atomic weight for combined helium is found to be 4.0032, which when multiplied by 52 gives 208.16 as the atomic weight of thorium-lead, in place of the value 208.06 which comes from the experimentally determined value of the atomic weight of thorium, together with the value of the packing effect as calculated from the energy change, as discussed above. On comparing experimental values alone it is found that 58 times 4.0018 is 232.105, while the experimental value for thorium is 232.12, or a difference of only six thousandths of one per cent. It therefore seems almost certain that the atoms of the thorium series are intra-atomic compounds of helium alone, that is their nuclei consist of alpha particles and negative electrons only. It is of interest to note that the highest experimental atomic weight for this thorio-lead as determined by Hönigschmid, is 207.90 ± 0.013, or 52×3.998, but it is almost certain that this atomic weight is somewhat too low, on account of the inclusion of another isotope.

Fully as good evidence can be presented in favor of the formulæ given for the atoms of the uranium disintegration series, for almost all of the atomic weights in the latter series can be obtained from those of the former by adding almost exactly 2.00, or 2.00 plus the atomic weight of helium (4.00). Thus the difference between the atomic weight of uranium and that of thorium is $4.00 + 2.055$, and while a part of the difference of 0.055 units may be accounted for by differences in the packing effects in the two nuclei, the whole of the deviation is small enough to be easily explained by the necessary errors in the atomic weight determinations. In the uranium-radium series two other atomic weights have been determined by accurate methods. Hönigschmid found the atomic weight of radium to be 225.97, which is extremely close to 226.00, while for uranium he found 238.175. After making allowance for the packing effect of 0.013 units, there is still a discrepancy of 0.19 units to be explained either by experimental error or by the inclusion of an unknown isotope in one or both. For radio-lead (radium G) his lowest determinations gave 206.06, while the similar determinations of Richards and Wadsworth gave 206.08. Since in even these last determinations ordinary lead was probably an impurity present in small amounts, the atomic weights as determined would undoubtedly have been very slightly smaller if the substance had been entirely pure.

[1] J. Am. Chem. Soc., *38*, 2613 (1916).

The accurately determined atomic weights in the radioactive series are summarized in Table IV.

TABLE IV.

Atomic Weights of Radioactive Atoms.

Atom.	Atomic Weight.	Deviation from a Whole Number.	Atomic Weight.
Uramium	238.175	+0.175	59×4.0030+2.00
Thorium	232.12	+0.12	58×4.0023
Radium	225.97	−0.03	56×3.9983+2.00
Radio-lead (Ra G)	206.07	+0.07	51×4.0014+2.00

Thus the heavy atoms as well as the light atoms have atomic weights which lie very close to whole numbers. The value obtained by Heuse for the atomic weight of helium is 4.002, and that of Taylor as recalculated by Guye is 3.998, while column 4 of the above table shows that the values of the atomic weight of intra-atomically combined helium as calculated on the basis of the hydrogen-helium hypothesis are: 4.003, 4.002, 4.001, and 3.998. The atomic weights of carbon and oxygen are 12.002 (according to Guye) and 16.00, which give 4.0007 and 4.0000 for helium, so the average packing effect when helium nuclei unite to form a complex nucleus is extremely small, while the same effect in the formation of helium from hydrogen is very large, amounting to 0.77 per cent., so as has already been stated the helium nucleus is extremely more stable than the more complex nuclei. Compared with the great difficulty of breaking up the helium nucleus it should be easy to disintegrate the more complex nuclei into helium, or into helium and hydrogen or an isotope of hydrogen in the case of the atoms of odd number. In the breaking up of such complex nuclei the only apparent difficulty is to get the energy into the small space occupied by the nucleus.

That the alpha and beta particles emitted in a radioactive change are shot out from the nucleus, has been indicated by Rutherford and Bohr. Recently Hackh in this REVIEW has given an interpretation of the accompanying changes which does not agree with that of the writer. Alpha particles are always shot out at a high speed, so the nucleus suffers a high speed recoil. Thus if the speed of the alpha particle is 20,000 miles per second, that of the nucleus would be nearly 400 miles per second. The nucleus travels at such a high rate of speed, though usually only for a short distance, that it undoubtedly shoots away from a part of its planetary electrons though the most recent work on the subjects seems to indicate that it retains just enough electrons to preserve its electrical neutrality. The loss of two positive charges from the nucleus reduces

the nuclear charge by 2, so that the atom which is formed contains 2 less planetary electrons, which means 2 less valence electrons, so the valence is reduced by 2. On the other hand, when a beta particle is shot out by the nucleus, the loss of one negative charge increases the positive charge of the nucleus by one, so that the atom to become electrically neutral picks up a negative planetary electron which goes into its valence shell, thereby increasing the positive valence by one. For a discussion of possible arrangements of the planetary electron papers, by Thomson,[1] Bohr,[2] Kossel,[3] Parson,[4] Lewis,[5] and Langmuir,[6] should be consulted. The writer has long been of the opinion that the facts of organic chemistry indicate a three-dimensional, rather than a plane arrangement of the planetary electrons.

1. Phil. Mag., 27, 757 (1914); 476, 857.
2. Ibid., *26*, 1, (1913); *29*, 332 (1915).
3. Ann. Physik, 49, 229 (1916).
4. Smithsonian Publications, 2371, Washington, (1915).
5. J. Am. Chem. Soc., *38*, 762 (1916).
6. Ibid., *41*, 868–934, 1543–9 (1919).
7. Ibid., *38*, pages 179 and 204 (1916); *39*, 856 (1916).

For a more complete set of references see papers by Harkins and Wilson, ibid., 37, 1367–1421, especially 1420–21.

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THE BOHR THEORY AND THE APPROXIMATE HARMONICS IN THE INFRA-RED SPECTRA OF DIATOMIC GASES.

BY EDWIN C. KEMBLE.

SYNOPSIS.

Infra-red spectra of diatomic gases; a quantum theory. The author's earlier theoretical *explanation of the occurrence of approximate harmonics* in the infra-red spectra of HCl, HBr and CO, based on the non-linearity of the law of force governing the relative displacement of the component atoms, encountered three difficulties: it did not explain the inexactness of the harmonics; it gave a wrong ratio for the asymmetry constants of the fundamental and harmonic bands; and it was in serious conflict with Kirchhoff's law. It is now shown that by *adopting Bohr's hypotheses* that the molecules possess a series of discrete, non-radiating states of vibration and that the frequencies radiated and absorbed are determined by the energy emitted or absorbed, a new explanation is obtained which seems to overcome the difficulties mentioned above. In connection with the discussion the author presents a full account of his *theory of the asymmetry* of the bands, which postulates a decrease in the frequency of vibration of a rotating diatomic molecule with increasing angular velocity, a consequence of the non-linearity of the law of force. It is found that the theory gives the observed value of the ratio of the asymmetry constants only if it is assumed that the minimum kinetic energy for vibratory motion is not finite as for rotary motion in the Bohr theory, but is zero.

Kirchhoff's law; suggested limitation. The author's theory of the structure of these band spectra is based on a theory which involves a minor contradiction to Kirchhoff's law since it leads to the conclusion that the ratio of the intensities of any two component parts of an absorption band is independent of the temperature. This suggests that Kirchhoff's law may not hold in such cases.

INTRODUCTION.

IN 1916 the writer published a theoretical paper[1] predicting the occurrence of weak harmonics to the principal absorption bands in the infra-red spectra of diatomic gases. The theory was based on the assumption that the form of the electromagnetic waves radiated or absorbed by an oscillating dipole must be related to the form of the vibration in the manner indicated by the classical electromagnetic theory. It was shown that, on account of the non-linearity of the law of force governing the relative displacement of the atoms of a diatomic molecule, vibrations of these atoms along their line of centers having the amplitudes called for by the quantum theory must depart considerably from the simple harmonic type. According to Fourier's theorem the

[1] PHYS. REV. (Ser. 2), 8, 1916 (701).

radiation emitted from such a vibrator should therefore consist of a harmonic series of wave-lengths. It was assumed that the entire series of emitted frequencies must also be absorbed. The infra-red absorption bands of diatomic gases, which are believed to have their origin in the atomic vibrations under consideration, should accordingly be accompanied by faint harmonics. As an example of the occurrence of such faint harmonics, the infra-red absorption bands of carbon monoxide were cited at the time, while a later paper[1] by Dr. J. B. Brinsmade and the writer reported the discovery of similar harmonic absorption bands in the infra-red spectra of HCl and HBr, which were held to constitute a verification of the theory.

There were, however, three difficulties in connection with the above explanation of the observations, viz., (*a*) the fact that the observed harmonics seemed not to be exact, the wave-length of the center in each case being from 0.025 μ to 0.045 μ greater than its calculated value, (*b*) the fact that the relation between the assymmetry constants of the fundamental and harmonic absorption bands in the HCl spectrum was not that predicted by the theory, and (*c*) the incompatibility of the theory itself with Kirchhoff's law. In the absence of an alternative explanation of the phenomena, and in view of the inherent plausibility of the explanation given above, the writer was inclined to attribute the discrepancies (*a*) and (*b*) to a slight error of unknown origin in the dispersion curve for quartz used in calculating the wave-lengths, and to assume that these harmonics constitute a *bona fide* exception to Kirchhoff's law. He now desires to report that the hypotheses adopted by Bohr in his theory of radiation and of atomic structure afford an alternative explanation of the observed phenomena which seems to avoid the above-mentioned difficulties.

THE APPLICATION OF BOHR'S HYPOTHESES TO RADIATION FROM VIBRATING DIATOMIC MOLECULES.

We proceed to the application of Bohr's hypotheses to the radiation from a vibrating diatomic molecule. The molecules are assumed to possess a series of discrete, non-radiating, steady, possible states of vibration. Let τ denote the number of any of these steady states, and let W_τ denote the corresponding energy of vibration. The law of force governing the motion being nonlinear, the frequency of vibration, ω, will depend upon the energy and therefore upon τ. In accordance with the earlier form of Planck's theory we assume that the energy of vibration is always an integral multiple of $h\omega$. (See supplementary note). Thus

$$W_\tau = \tau h\omega, \qquad \tau = (0), 1, 2, 3, \cdots. \quad (1)$$

[1] J. B. Brinsmade and E. C. Kemble, Proc. Nat. Acad. Sci., 3, 1917 (420).

According to the Bohr theory the angular momentum of an electron attached to a single hydrogen atom cannot be reduced below the minimum value $h/2\pi$. The observed structure of the infra-red absorption bands of HCl indicates that the above remark is also true of the angular momentum of a diatomic molecule.[1] These considerations create the presumption that the energy of any vibratory degree of freedom as well as that of any rotational degree of freedom must always be greater than zero, in accordance with which zero should be eliminated from the list of the possible values of τ in the above equation. There is some evidence in the present theory, however, that such a generalization is incorrect, and the question will accordingly be left open.

With Bohr we add the hypothesis that the frequency of the radiation emitted or absorbed by the molecule in passing from the steady state τ_1 to the steady state τ_2 is given by the relation

$$h\nu = |\,(W_{\tau_2} - W_{\tau_1})\,|. \qquad (2)$$

Combining these assumptions, we obtain the following expression for the radiation frequencies emitted or absorbed:

$$\nu = |\,(\tau_2\omega_{\tau_2} - \tau_1\omega_{\tau_1})\,|. \qquad (3)$$

If the frequency of vibration were completely independent of the amplitude, as in the case of an ideal linear oscillator, the frequencies emitted and absorbed would all be integral multiples of ω. If the frequency of vibration is nearly independent of the amplitude, the frequencies of the radiation emitted and absorbed will be approximately integral multiples of the frequency of vibration for small amplitudes. This theory, therefore, like the other, predicts the occurrence of (approximate) harmonics, though it gives them a different interpretation. The fundamental absorption band is due to the molecules jumping from the first of the steady states of vibration to the second (at ordinary temperatures the number of molecules normally in the second steady state is infinitesimal), while the first harmonic is due to the molecules jumping from the first steady state to the third.

Let us now see how the present theory meets the difficulties encountered by the former.

WAVE-LENGTHS OF "HARMONICS."

The fact that the wave-length of the center of the "harmonic" band is in each case observed to be a little more than half of the wave-length of the fundamental fits perfectly with the new theory. We may assume as a first approximation for small amplitudes that the equation

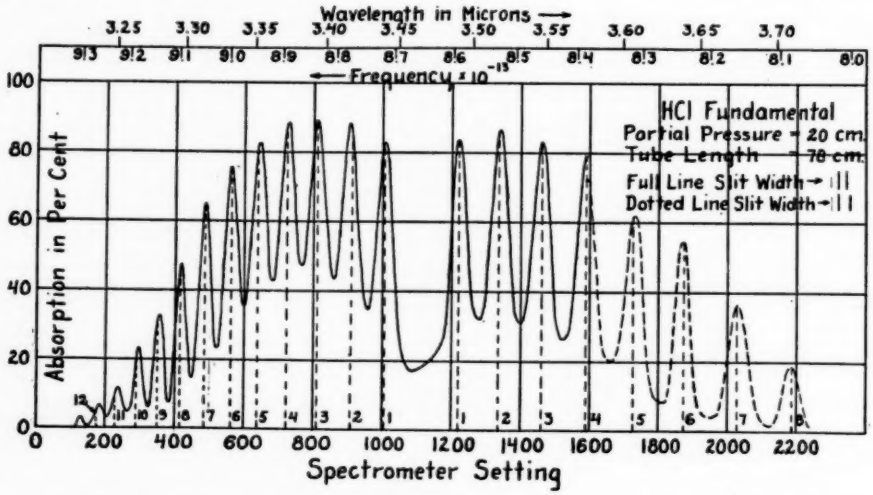
[1] Brinsmade and Kemble, l. c., p. 425.

of motion may be thrown into the form[1]

$$m\frac{d^2z}{dt^2} = -kz - k_2z^2. \tag{4}$$

In this case, whatever the sign of k_2, the frequency of vibration decreases when the amplitude increases.[4] Consequently the energy of a molecule should increase by a smaller amount when the molecule passes from the second steady state to the third than when it passes from the first to the second, and the frequency absorbed in passing from the first steady state to the third should be a little less than twice that absorbed in passing from the first to the second.

In order to show that the present theory is in qualitative agreement with the observed relative asymmetry of the two infra-red absorption


Wavelength in Microns →
3.25 3.30 3.35 3.40 3.45 3.50 3.55 3.60 3.65 3.70
9|3 9|2 9|1 9|0 8|9 8|8 8|7 8|6 8|5 8|4 8|3 8|2 8|1 8|0
← Frequency x 10^-13
HCl Fundamental
Partial Pressure = 20 cm.
Tube Length = 78 cm.
Full Line Slit Width → | | |
Dotted Line Slit Width → | | |
Absorption in Per Cent
0 20 40 60 80 100
0 200 400 600 800 1000 1200 1400 1600 1800 2000 2200
Spectrometer Setting

bands of HCl it is necessary to indulge in some mathematical analysis. The writer has never published a full account of his theory of the asymmetry of the infra-red absorption bands of diatomic gases[2] and therefore welcomes this opportunity to present that theory in complete form.

THE ASYMMETRY OF THE INFRA-RED ABSORPTION BANDS OF DIATOMIC GASES.

According to the elementary theory of the structure of the infra-red absorption bands of diatomic gases given by Bjerrum[3] each of these

[1] Reference No. 1, p. 708.

[2] The theory was first stated in an unpublished paper bearing the title "The Infra-red Absorption Bands of Gases and the Application of the Quantum Theory to Molecular Rotations" read before the American Physical Society on December 28, 1916. A brief statement of the essentials of the theory is to be found in the paper by Brinsmade and Kemble cited above.

[3] N. Bjerrum, Nernst Festschrift, Halle, 1912; Verh. d. D. Physik. Ges., 16, 1914 (640).

bands owes its width primarily to the effect of the molecular rotations and should be composed of a double series of elementary bands or quantum lines. (These elementary bands are themselves of quite appreciable breadth, but in order to distinguish them from the composite band which they unite to form, it will be convenient to designate them in the remainder of this paper as "quantum lines.") The molecules are assumed to vibrate with a common frequency ω. The radiation emitted and absorbed by the molecules which rotate with the frequency ν_r is divided between the frequencies $\omega + \nu_r$ and $\omega - \nu_r$. Consequently the molecules having any given angular velocity give rise to a pair of narrow absorption lines whose separation on the frequency scale is twice the frequency of the rotation. According to the quantum theory the frequencies of rotation must all be integral multiples of a certain basic frequency which we denote by the symbol ν_1. Hence the only frequencies radiated or absorbed are those given by the formula

$$\nu = \omega \pm p\nu_1, \qquad p = 1, 2, 3, \cdots. \quad (5)$$

Thus the quantum lines corresponding to different values of p should be equally spaced. Since the two absorption lines corresponding to each value of p are due to the same group of molecules, they should be of nearly equal intensity, while the intensities of the lines corresponding to different values of p should vary with the numbers of molecules in the corresponding groups. Consequently the large band of which these lines are the components should have the general appearance of a symmetrical doublet.

The accompanying figure shows the appearance of the principal band in the infra-red spectrum of HCl as observed by Dr. Brinsmade and the writer.[2] Instead of being equally spaced, the quantum lines are obviously closer together on the high frequency side and it is evident that if the band is observed with a spectrometer of low resolving power it will appear to be an asymmetric doublet, the high frequency maximum being the more intense. This group of lines and the approximately harmonic group in the same spectrum are the only infra-red absorption bands in the spectra of the diatomic gases which have been resolved into their elementary components, but the infra-red absorption bands of the other diatomic gases are similarly asymmetric doublets.

In the writer's opinion the asymmetry is due to a decrease in the frequency of vibration with increasing angular velocity. This decrease results from the nonlinearity of the law of force which governs the vibratory motion.

In order to reduce the above hypothesis to quantitative form, we

proceed to formulate the equations of motion of the rotating and vibrating molecule. It will be assumed that the masses of the two atoms, m_1 and m_2, are concentrated in the nuclei. Let ζ denote the distance between the atomic centers and let

$$m = m_1 m_2/(m_1 + m_2).$$

Let θ denote the angle between the line of the atomic centers and any fixed line in the plane of the motion. With this notation the expression for the kinetic energy of the system is readily reduced to the form

$$T = \frac{m}{2}\left[\left(\frac{d\zeta}{dt}\right)^2 + \zeta^2\left(\frac{d\theta}{dt}\right)^2\right]. \tag{6}$$

Denoting the potential energy by $\Phi(\zeta)$ and setting up Lagrange's equations, we have

$$\frac{d}{dt}(m\dot{\zeta}) - m\zeta\dot{\theta}^2 + \Phi'(\zeta) = 0 \tag{7}$$

and

$$\frac{d}{dt}(m\zeta^2\dot{\theta}) = 0. \tag{8}$$

Equation (8) gives rise to the statement of the constancy of the angular momentum. This may be written

$$m\zeta^2\dot{\theta} = m\zeta_0^2\Omega_0, \tag{9}$$

where ζ_0 is assumed to be the distance between the nuclei when the molecule is in equilibrium and at rest, while Ω_0 is the angular velocity of the moving molecule when ζ passes through the value ζ_0. Substituting from (9) into (7) we obtain the differential equation for the vibratory motion:

$$m\frac{d^2\zeta}{dt^2} = -\Phi'(\zeta) + m\frac{\Omega_0^2\zeta_0^4}{\zeta^3}. \tag{10}$$

Let U denote the total energy of vibratory and rotational motion, and let ζ_1 and ζ_2 denote the minimum and maximum values of ζ. Integration of equation (10) then gives the following expression for the period of the vibration:

$$\tau = \sqrt{2m}\int_{\zeta_1}^{\zeta_2} \frac{d\zeta}{\sqrt{U - \Phi(\zeta) - \dfrac{m\Omega_0^2\zeta_0^4}{2\zeta^2}}}. \tag{11}$$

Obviously ζ_1 and ζ_2 are roots of the equation

$$U - \Phi(\zeta) - \frac{m\Omega_0^2\zeta_0^4}{2\zeta^2} = 0. \tag{12}$$

Ω_0 can be identified with the mean angular velocity of the molecule

without appreciable error and equation (11) shows that the period of vibration is a function of Ω_0. It also shows that if τ, or its reciprocal, the frequency of vibration, ω, is expanded into a power series in Ω_0, the coefficients of the odd powers must vanish, since a reversal of the sign of Ω_0 cannot affect the value of τ. Denoting the frequency of rotation by $p\nu_1$ and the frequency of vibration for zero angular velocity by ω_0, we may therefore write as a first approximation

$$\omega = \omega_0 - ap^2\nu_1^2. \tag{13}$$

The coefficient a is a function of the total vibrational energy W. It will be shown later on that in general we may expect a to be positive.

If we adopt the fundamental hypothesis of the writer's earlier work, which identifies the frequency of vibration of the molecule with the mean of the two radiation frequencies absorbed (or radiated), and combine equations (5) and (13), we obtain

$$\nu = \omega_0 - ap^2\nu_1^2 \pm p\nu_1. \tag{14}$$

This is the equation for the position of the quantum lines given in the writer's former brief statement of the theory of asymmetry.[1] If the values of ω_0, a, and ν_1 are properly chosen, the formula gives the frequencies of the quantum lines in the HCl fundamental with considerable accuracy (cf. the vertical dashed lines in the figure[2]).

The positions of the lines in a true harmonic should be given by

$$\nu = 2(\omega_0 - ap^2\nu_1^2) \pm p\nu_1. \tag{14a}$$

Equation (14a) is of the same form as (14) and gives the frequencies of the quantum lines in the observed harmonic correctly if the values of the constants ω_0 and a are readjusted. No readjustment of the value of ν_1 is necessary.

Equation (5), however, does not fit with the fundamental hypotheses regarding the nature of the process of radiation on which the present paper is based. In order to bring the theory of asymmetry into line with the Bohr theory we must assume that equation (3) gives the mean of the two frequencies emitted and absorbed by any one group of molecules.[3] Confining our attention to the process of absorption, we replace equation (5) by

$$\nu = \tau_2\omega_{\tau_2} - \tau_1\omega_{\tau_1} \pm p\nu_1, \qquad \begin{cases} p = 1, 2, 3, \cdots, \\ \tau_2 > \tau_1. \end{cases} \tag{15}$$

[1] Brinsmade and Kemble, l. c., p. 424.

[2] The consistent discrepancy in the outermost quantum lines on the high frequency side is completely eliminated without the introduction of fresh arbitrary constants if the change in the moment of inertia due to the expansion of the molecule with increasing angular velocity is taken into account.

[3] An equivalent assumption has been used by Bohr to explain the Zeemon effect. Cf. Phil. Mag., 27, 1914 (520).

Since the frequency of vibration depends on the angular velocity and on the energy of vibration, ω is to be regarded as a function of τ and p. Moreover, the constant a is a function of τ. We therefore introduce the notation

$$\omega \equiv \omega(\tau, p);$$
$$a \equiv a(\tau).$$

Equation (13) becomes

$$\omega(\tau, p) = \omega(\tau, 0) - a(\tau)p^2\nu_1^2. \tag{16}$$

Combining (15) and (16), we obtain

$$\begin{aligned}\nu = {} & \tau_2[\omega(\tau_2, 0) - a(\tau_2)p^2\nu_1^2] \\ & - \tau_1[\omega(\tau_1, 0) - a(\tau_1)p^2\nu_1^2] \pm p\nu_1.\end{aligned} \tag{17}$$

Let $N(\tau_1, \tau_2)$ and $\mathfrak{A}(\tau_1, \tau_2)$ be defined by the equations

$$\begin{aligned}N(\tau_1, \tau_2) &\equiv \tau_2\omega(\tau_2, 0) - \tau_1\omega(\tau_1, 0), \\ \mathfrak{A}(\tau_1, \tau_2) &\equiv \tau_2 a(\tau_2) - \tau_1 a(\tau_1).\end{aligned} \tag{18}$$

Then (17) becomes

$$\nu = N(\tau_1, \tau_2) - \mathfrak{A}(\tau_1, \tau_2)p^2\nu_1^2 \pm p\nu_1. \tag{19}$$

This equation is of the same form as (14) and consequently gives the positions of the lines in either of the HCl bands with equal accuracy.

The specific expressions for N and $\mathfrak{A}$ for the fundamental and first harmonic differ according as we assume that zero is or is not a possible value of τ. If it is not, $\tau_1 = 1$ and $\tau_2 = 2$ for the fundamental. Thus

$$\begin{aligned}N &= 2\omega(2, 0) - \omega(1, 0), \\ \mathfrak{A} &= 2a(2) - a(1).\end{aligned} \tag{20}$$

In the case of the first harmonic we should then have $\tau_1 = 1$ and $\tau_2 = 3$. Denoting the values of N and $\mathfrak{A}$ for the first harmonic by the symbols N' and $\mathfrak{A}'$, we obtain

$$\begin{aligned}N' &= 3\omega(3, 0) - \omega(1, 0), \\ \mathfrak{A}' &= 3a(3) - a(1).\end{aligned} \tag{21}$$

If, on the other hand, we adopt the alternative hypothesis that zero is a possible value of τ, the above equations become

$$\begin{aligned}N &= \omega(1, 0); \\ N' &= 2\omega(2, 0); \\ \mathfrak{A} &= a(1); \\ \mathfrak{A}' &= 2a(2).\end{aligned} \tag{22}$$

In either case, if a were independent of the energy of vibration, $\mathfrak{A}'$

would be equal to $2\mathfrak{A}$. This relation is the same as that called for by the old theory and does not agree with experiment, since the observed value of the ratio of the asymmetry constants $\mathfrak{A}'$ and $\mathfrak{A}$ is a little less than 1.5. On the other hand, if a decreases regularly as the energy of vibration increases, it is to be expected in either case that the ratio of $\mathfrak{A}'$ to $\mathfrak{A}$ will be less than 2.

In order to justify fully the present revised theory of the structure of these infra-red absorption bands, it would be necessary to derive the observed values of the constants N, N', $\mathfrak{A}$, and $\mathfrak{A}'$ on the basis of a plausible form for the potential energy function Φ. Mathematical difficulties, however, stand in the way of such a complete solution of the problem, and for the present we must content ourselves with showing that the observed values of the constants mentioned are not unreasonable. To that end we shall assume a simple form for the potential energy function and shall study the variation in the frequency of vibration with the angular velocity and with the vibrational energy on the basis of the restricting hypothesis that the amplitude of the vibrations is small.

All that we can reasonably feel sure of in regard to the law of force which governs the motion of the atoms is that it is asymmetric in that the potential energy increases more rapidly when the atoms are compressed together than when they are drawn apart. A simple formula having the asymmetry suggested is obtained if the force is assumed to be composed of a constant attraction combined with a repulsion varying inversely as the nth power of the distance between the nuclei. The net repulsive force between the atomic centers will then be given by an expression of the form

$$-\Phi'(\zeta) = \alpha\zeta^{-n} - \beta, \tag{23}$$

where α and β are constants.

Since the force reduces to zero when ζ equals ζ_0,

$$\beta = \alpha/\zeta_0{}^n.$$

Equation (10) becomes

$$m\frac{d^2\zeta}{dt^2} = \alpha\left[\frac{1}{\zeta^n} - \frac{1}{\zeta_0{}^n}\right] + \frac{m\Omega_0{}^2\zeta_0{}^4}{\zeta^3}. \tag{24}$$

In order to integrate (24) we will throw it into the form (4) by means of approximations. Consider first the case where the angular velocity is zero. In this case it is convenient to expand $1/\zeta^n$ and $1/\zeta^3$ into power series about the point $\zeta = \zeta_0$. Let

$$\xi = \zeta - \zeta_0.$$

Then (24) is readily transformed into

$$m\frac{d^2\xi}{dt^2} = -\frac{\alpha n}{\zeta_0^{n+1}}\cdot\xi + \frac{\alpha n(n+1)}{2\zeta_0^{n+2}}\cdot\xi^2 + \cdots. \tag{25}$$

Neglecting the terms containing the cube and higher powers of ξ, we can throw (25) into the form (4) by establishing the relationships

$$k = \alpha n/\zeta_0^{n+1}; \tag{26a}$$

$$k_2 = -\alpha n(n+1)/2\zeta_0^{n+2}. \tag{26b}$$

According to Seeliger[1] the following equations constitute an approximate solution of (4):

$$\xi = A'\cos 2\pi\omega_0 t + A''\cos 4\pi\omega_0 t + \text{const.}, \tag{27a}$$

$$A' = A\left(1 + \frac{Ak_2}{3k}\right), \tag{27b}$$

$$A'' = A^2k_2/6k, \tag{27c}$$

$$\omega_0' = \frac{1}{2\pi}\sqrt{k/m}, \tag{27d}$$

$$\omega_0 = \omega_0'\left[1 - \frac{5}{12}A^2\left(\frac{k_2}{k}\right)^2\right]. \tag{27e}$$

In case the angular velocity is not zero, the molecule expands under the influence of centrifugal force, so that the equilibrium value of ζ changes from ζ_0 to ζ_1, where ζ_1 is a root of the equation

$$\alpha\left(\frac{1}{\zeta^n} - \frac{1}{\zeta_0^n}\right) + \frac{m\Omega_0^2\zeta_0^4}{\zeta^3} = 0. \tag{28}$$

It is convenient to introduce the quantity $\Delta\zeta$ defined by the equation

$$\Delta\zeta = \zeta_1 - \zeta_0.$$

Expanding the left-hand member of equation (28) in series, neglecting terms containing the squares and higher powers of $\Delta\zeta$, and solving for $\Delta\zeta$, we obtain the approximate value

$$\Delta\zeta = \frac{m\Omega_0^2\zeta_0}{\dfrac{\alpha n}{\zeta_0^{n+1}} + 3m\Omega_0^2}.$$

By the introduction of the frequency of rotation ν_r and by the use of equations (26a) and (27d) the above can be reduced to

$$\Delta\zeta = \frac{\zeta_0\nu_r^2}{\omega_0'^2 + 3\nu_r^2}.$$

Since the frequency of rotation ν_r is for all cases under consideration

[1] R. Seeliger, Verh. d. D. Physik. Ges., 16, p. 1042, 1914.

quite small compared with the frequency of vibration, we can neglect $3\nu_r^2$ in comparison with $\omega_0'^2$. Hence

$$\Delta\zeta = \zeta_0\nu_r^2/\omega_0'^2. \tag{29}$$

Now let

$$\xi = \zeta - \zeta_1.$$

Expanding in series about the point ζ_1 and discarding higher order terms, we throw (24) into the form

$$m\frac{d^2\xi}{dt^2} = -\left[\frac{\alpha n}{\zeta_1{}^{n+1}} + \frac{3m\Omega_0{}^2\zeta_0{}^4}{\zeta_1{}^4}\right]\xi + \left[\frac{\alpha n(n+1)}{2\zeta_1{}^{n+2}} + \frac{6m\Omega_0{}^2\zeta_0{}^4}{\zeta_1{}'}\right]\xi^2. \tag{30}$$

Let k' and k_2' denote the values of k and k_2 when Ω_0 does not vanish.

$$k' = \frac{\alpha n}{\zeta_1{}^{n+1}} + \frac{3m\Omega_0{}^2\zeta_0{}^4}{\zeta_1{}^4}$$

$$= \frac{\alpha n}{\zeta_0{}^{n+1}} + 3m\Omega_0{}^2 - \Delta\zeta\left[\frac{\alpha n(n+1)}{\zeta_0{}^{n+2}} + \frac{12m\Omega_0{}^2}{\zeta_0}\right].$$

$$-k_2' = \frac{\alpha n(n+1)}{2\zeta_1{}^{n+2}} + \frac{6m\Omega_0{}^2\zeta_0{}^4}{\zeta_1{}^5}$$

$$= \frac{\alpha n(n+1)}{2\zeta_0{}^{n+2}} + \frac{6m\Omega_0{}^2}{\zeta_0} - \frac{\Delta\zeta}{\zeta_0{}^2}\left[\frac{\alpha n(n+1)(n+2)}{2\zeta_0{}^{n+1}} + 30m\Omega_0{}^2\right].$$

By means of further approximations and with the help of equations (26*a*), (27*d*), and (29) the above expressions for k' and k_2' can be reduced to

$$k' = 4\pi^2 m\omega_0'^2\left[1 - (n-2)\frac{\nu_r^2}{\omega_0'^2}\right], \tag{31}$$

$$k_2' = -\frac{4\pi^2 m\omega_0'^2}{\zeta_0}\left[\frac{n+1}{2} - \left\{\frac{(n+1)(n+2)}{2} - 6\right\}\frac{\nu_r^2}{\omega_0'^2}\right]. \tag{32}$$

Hence

$$k_2'/k' = -\frac{n+1}{2\zeta_0}\left[1 - \left\{4 - \frac{12}{n+1}\right\}\frac{\nu_r^2}{\omega_0'^2}\right]. \tag{33}$$

Let ω denote the frequency of vibration corresponding to the angular frequency ν_r. Then

$$\omega = \frac{1}{2\pi}\sqrt{\frac{k'}{m}}\left[1 - 5/12\,A^2\left(\frac{k_2'}{k'}\right)^2\right]$$

$$= \omega_0'\left\{1 - \frac{5}{48}\left(\frac{A}{\zeta_0}\right)^2(n+1)^2 - \left[\frac{n-2}{2} - \left(8 - \frac{24}{n+1}\right)\frac{5}{48}(n+1)^2\left(\frac{A}{\zeta_0}\right)^2\right]\frac{\nu_r^2}{\omega_0'^2}\right\}. \tag{34}$$

Comparing equations (13) and (34) we see that

$$a = \frac{1}{\omega_0'}\left[\frac{n-2}{2} - \left(8 - \frac{24}{n+1}\right)\frac{5}{48}(n+1)^2\left(\frac{A}{\zeta_0}\right)^2\right]. \qquad (35)$$

It is to be expected on the basis of the attempts which have been made to formulate a law governing the mutual repulsion of whole molecules that n will have a value between 5 and 15. That being the case, it will be observed that for small values of A (which is a measure of the amplitude of the vibration) a is a positive quantity whose value decreases with the energy of vibration. A qualitative agreement between the observed values of $\mathfrak{A}$ and $\mathfrak{A}'$ and the equations (20) and (21), or (22) is thus established.

The writer has shown elsewhere that in the case of HCl the ratio A/ζ_0 should be in the neighborhood of 0.12 when $\tau = 1$. The above approximate equations are certainly not valid for such large amplitudes of vibration as this, but it is of interest to apply them even out of the range in which they are properly applicable.

The square of A is roughly proportional to the energy of vibration, which, in turn, is roughly proportional to τ. Hence we may substitute $(0.12)^2\tau$ for A/ζ_0 in (35). The observed values of N and N' are 8.655×10^{-14} and $2 \times 8.49 \times 10^{-14}$ respectively, from which we may assume, on the basis of equations (22), that 8.8×10^{-14} is not far from the correct value of $\omega(0, 0)$, or ω_0'. Substituting these values into (35) and giving n the value 7.5, we obtain

$$a = (3.125 - 0.638\tau) \times 10^{-14}.$$

Equations (22), based on the assumption that the vibrational energy may be reduced to zero, then give $\mathfrak{A} = 2.5 \times 10^{-14}$ and $\mathfrak{A}' = 3.7 \times 10^{-14}$. The observed values of these constants are $\mathfrak{A} = 2.55 \times 10^{-14}$ and $\mathfrak{A}' = 3.7 \times 10^{-14}$ respectiveiy, so that the agreement is excellent. On the other hand it is not possible to choose any value of n which will give good values of either $\mathfrak{A}$ or $\mathfrak{A}'$ if we assume that equations (20) and (21) are correct.

The internal evidence of our theory therefore favors the hypothesis that for vibrational motion zero is one of the possible values of τ. In other words, there is no "zero-point energy" for vibrational degrees of freedom such as that which the Bohr theory assumes for the rotational degrees of freedom. Too much weight should not be attached to this result, however, since the equations on which it is based are admittedly inaccurate and give excessively large differences between the frequencies N' and $2N$.

KIRCHHOFF'S LAW.

The problem of giving quantitative proof that the present extension of Bohr's theory is in harmony with Kirchhoff's law is substantially equivalent to the problem of deriving Planck's radiation formula from the theory in question, and it involves the introduction of hypotheses which are outside the scope of the present paper. The writer will therefore content himself here with a qualitative discussion of the relation of the theory to Kirchhoff's law in the hope that he may later have the privilege of taking up the problem in a quantitative manner.

Kirchhoff's law rests on the proposition that the ratio of the coefficient of emission of any medium for the frequency ν to its coefficient of absorption for the same frequency when in a state of thermodynamic equilibrium is equal to the specific intensity of black radiation for the same temperature and frequency divided by the square of the index of refraction.[1] If we assume (following in the footsteps of Planck) that we have to do with a gaseous medium of very low density, we may call the index of refraction unity. Denoting the coefficients of emission and absorption by ϵ_ν and α_ν respectively, and the intensity of black radiation by K_ν, we have

$$\frac{\epsilon_\nu}{\alpha_\nu} = K_\nu.$$

Let ν' denote any other frequency. Then

$$\frac{\epsilon_{\nu'}}{\alpha_{\nu'}} = K_{\nu'},$$

and by Planck's radiation law

$$\frac{\epsilon_\nu}{\epsilon_{\nu'}} \div \frac{\alpha_\nu}{\alpha_{\nu'}} = \left(\frac{\nu}{\nu'}\right)^3 \left[\frac{e^{h\nu'/kT} - 1}{e^{h\nu/kT} - 1}\right]. \tag{36}$$

Equation (36) must be satisfied for any two frequencies ν and ν', if Kirchhoff's law is to be satisfied, and conversely we may apply (36) to the theory of harmonics as a test of its compatibility with Kirchhoff's law.

In making this test, we may, to begin with, neglect the broadening of the absorption and emission bands by molecular rotations and by the Doppler effect. ϵ_ν and $\epsilon_{\nu'}$ may then be replaced by the integrated intensities of the fundamental and harmonic emission bands, while α_ν and $\alpha_{\nu'}$ are replaced by the corresponding intensities of the absorption bands. It should be observed that if we replace ν' by 2ν the right-hand member of (36) decreases from infinity for very small values of the temperature T to one fourth for very large values of T. Consequently

[1] Cf. Planck's "Heat Radiation" (trans. by Masius), p. 35.

either the ratio of the emission coefficients $\epsilon_\nu \epsilon_{\nu'}$ must decrease greatly with increasing temperature or the ratio of the absorption coefficients $\alpha_\nu \alpha_{\nu'}$ must increase to the same extent.

Now according to the writer's earlier theory of harmonics the ratio of the intensities of the fundamental and harmonic bands was independent of the temperature for both the absorption and emission processes, in complete disaccord with (36). The present theory, on the other hand, provides for a large temperature variation in the relative emission from the two bands, although the ratio of the absorption percentages should be independent of the temperature. This is because the fundamental and harmonic emission bands have their origin in *different* groups of molecules, the relative numbers in which vary with the temperature. Thus, at the lowest temperatures the number of molecules in the second steady state is infinite compared with the number in the third, while at extremely high temperatures the numbers approach equality and the *relative* intensity of the fundamental emission band decreases correspondingly.

The above fact establishes a qualitative agreement between our new theory of harmonics and Kirchhoff's law and shows that the new theory meets all the difficulties encountered by the old in a qualitative manner, at least. It should be observed, however, that there is a minor contradiction to Kirchhoff's law involved in the Bjerrum theory of the structure of the infra-red absorption and emission bands upon which the present work is in part based. For if we let ν and ν' in equation (36) denote the frequencies of the two quantum lines in one of these bands which are due to the group of molecules having any one of the possible angular velocities, we get into the same trouble as in the writer's first theory of harmonics. The two elementary absorption bands are due to the same group of molecules and the two emission bands are due to the same group. Consequently the ratio of the intensities of the absorption bands and the ratio of the intensities of the two emission bands should apparently each be independent of the temperature. As the Bjerrum theory is very well established the above consideration seems to force the conclusion that, while equation (36) may be, and probably is, correct when applied to regions of the spectrum which are far apart, it cannot hold when applied to narrow strips of the spectrum which are very close together. In other words, Kirchhoff's law and the rule that the ratio of the intensity of radiation inside any body or substance in thermodynamic equilibrium to the square of the index of refraction is a universal function of the temperature and frequency, while approximately correct as broad generalizations, are not strictly true when applied to the comparison of closely adjacent portions of the spectrum.

SUPPLEMENTARY NOTE.

Since placing the above paper in the hands of the publishers, my attention has been called to the formulation of the quantum condition for the determination of the steady states of motion by W. Wilson (Phil. Mag., 29, pp. 795–802, June, 1915), and the arrival of the long delayed copies of the Annalen der Physik for 1916 has put into my hands the independent formulation of this same hypothesis by Sommerfeld, together with his brilliant explanation of the complex structure of the lines in the spectra of hydrogen and ionized helium by its aid.

The quantum condition in question takes the form of the requirement that certain of the generalized coördinates of the atomic or molecular systems in question shall satisfy equations of the form

$$\int p dq = \tau h,$$

where p is the momentum corresponding to the coördinates q, h is Planck's constant, τ is an integer, and the integration is to be extended over a complete cycle of values of q. Applying this condition to the vibration of a diatomic molecule we obtain

$$\int m\dot{\zeta} d\zeta = 2\int T dt = \tau h,$$

or

$$\overline{T} = \frac{\tau}{2} h\omega.$$

Here, as in the text above, T and ω denote the kinetic energy and the vibrational frequency respectively.

If we assume, as a first approximation, that the mean values of the kinetic and potential energies are sensibly equal, we obtain equation (1) above.

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REFLECTION AND TRANSMISSION OF ULTRA-VIOLET LIGHT BY SODIUM AND POTASSIUM.

BY MABEL KATHERINE FREHAFER.

SYNOPSIS.

Reflecting power of K and Na, for wavelengths from 0.25 to 0.55 μ. (1) *Normal incidence* (10°). *Opaque mirrors* in contact with fused quartz were tested with monochromatic light from a mercury arc. A sodium photoelectric cell was used to compare the intensities of incident and reflected beams. It was found that sodium maintains a remarkably high reflecting power throughout the ultra-violet, increasing slightly from a flat minimum near 3600A to 80 per cent. at 2536A. The reflecting power of potassium on the contrary decreases rapidly with the wavelength, reaching the very low value of 11 per cent. at 2536A. *A thin film of potassium* deposited and kept at −190° C. gave a curve of the same form. Among the metals so far investigated in the ultra-violet, therefore, sodium and potassium have respectively the highest and lowest reflecting powers. (2) *Polarized light at 45° incidence.* The ratio of the reflecting powers for light polarized with the electric vector respectively parallel and perpendicular to the plane of incidence, was found for both sodium and potassium to have a maximum value near 3650A. There is also a common minimum at about 3341A which is far more pronounced in the case of sodium.

Transmitting power of K and Na films for wave-lengths from 0.25 to 0.55 μ. Films deposited on quartz and on glass at liquid-air temperatures were studied while still cold by the use of a special apparatus and compared with the ordinary colloidal films prepared at room temperature. The results are shown graphically. Under comparable conditions, the transmitting power of potassium is considerably greater than that of sodium.

Thin films of K and Na deposited at −190° C. on quartz have a metallic *appearance;* on being warmed a thin film becomes peppered with holes and an opaque film loses its luster.

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Arrangement of Apparatus and Experimental Procedure with Mirrors
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Summary.

A STUDY of the reflecting power of the alkali metals in the ultra-violet is of special interest in connection with the selective photo-electric effect. Since this property of metals probably points to a resonance phenomenon, it seems possible that a knowledge of the optical properties may throw some light on the mechanism of this effect. The relation between the electron emission and the light absorption in the selective effect does not appear to be a direct linear one, such as seems to exist in the normal effect for a given wave-length.

The alkali metals, especially sodium and potassium, are highly reflecting in the visible spectrum, with large extinction coefficients and extremely small refractive indices. Drude's[1] values of the index of refraction of sodium and of the extinction coefficient, obtained by analyzing the state of polarization of yellow light reflected from the surface of the molten metal, were the only data available until the work of R. W. and R. C. Duncan[2] who, using Drude's method, determined the optical properties of both sodium and potassium as a function of the wave-length in the visible region. The metals were used in the solid form backed by glass. The first direct method for the determination of the reflecting powers of these metals was used by Nathanson[3] for sodium, potassium and rubidium, with white light and monochromatic polarized light for the region 6409–4546 Å. He also used the solid metal backed by glass. The intensity of the light was measured by means of a photoelectric cell, connected to an electrometer.

The well-known "selective effect" of the alkali metals and a few other metals offers a particularly promising field of research for the relations existing between the ejected electrons and the atoms. It was with the hope of throwing some light on this subject that this investigation of the reflecting powers of sodium and potassium through the regions in which the selective effect occurs has been attempted. Elster and Geitel[4] were the first to show that the selective effect is directly concerned with the position which the electric vector in the incident light has relative to the metallic surface; that is, the photoelectric current is a maximum when the plane of polarization is perpendicular to the plane of incidence (*i.e.*, the electric vector is in the plane of incidence), and is a minimum when these planes are parallel (*i.e.*, the electric vector is at right angles to the plane of incidence). Pohl and Pringsheim[5] have

[1] Drude, Annalen der Physik, 64, 159, 1898.

[2] R. W. and R. C. Duncan, PHYSICAL REVIEW, 36, 294, 1913.

[3] Nathanson, Astrophysical Journal, 44, 137, 1916.

[4] Elster and Geitel, Annalen der Physik, 52, 540, 1894; 55, 684, 1895; 61, 445, 1897.

[5] Pohl, Physikalische Zeitschrift, 10, 542, 1909. Pohl, Deutsche Physikalische Gesellshaft, 11, 339 and 609, 1909. Pohl and Pringsheim, Deutsche Physikalische Gesellshaft, 12, 215 and 349, 1910.

determined the photoelectric current as a function of the wave-length, both for $E_{||}$ and $E_{\perp}$, as well as for unpolarized light incident at some angle different from zero (corresponding to $E_{||}$). These results have been embodied in the familiar diagram reproduced here.

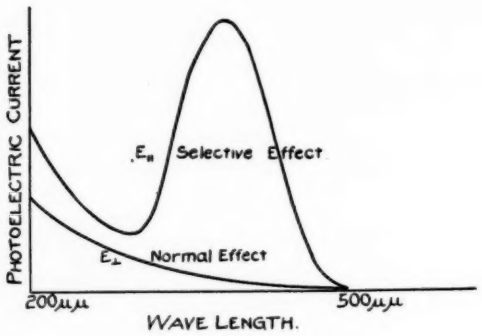

Fig. 1.

The ordinates represent the amount of electron emission for equal amounts of energy in the exciting light.

The ratio $E_{||}/E_{\perp}$ gives a curve similar to $E_{||}$ and yields the same value of λ for the maximum of the selective effect.

The conclusion from their work and that of others is that when the electric vector in the incident light has a component perpendicular to the metal surface illuminated, the resulting electron emission, called the selective effect, increases enormously for a number of elements, the maximum values occurring at definite values of λ. For sodium and potassium these values are as follows:

Na:	$\lambda =$	340 $\mu\mu$ (Pohl and Pringsheim)[1]
		360 $\mu\mu$ (Richardson and Compton)[2]
K:		436 $\mu\mu$ (Pohl and Pringsheim)[3]
		440 $\mu\mu$ (Braun)[4]

A study of the velocities of the electrons emitted in the normal and selective effects was made by Hughes,[4] but these values proved to be only slightly different from each other. The difference in the mechanism of the normal and selective effects is still left undetermined—beyond the fact that the former suggests an action of free electrons, the latter of electrons in the atoms, of frequencies characteristic of the metal.

The work of Richardson and Compton[7] has shown a maximum photo-

[1] Pohl and Pringsheim, Deutsche Physikalische Gesellshaft, 14, 49, 1912.

[2] Richardson and Compton, Philosophical Magazine, 26, 549, 1913.

[3] Braun, Dissertation, Bonn, 1906.

[4] Hughes, Philosophical Magazine, 31, 100, 1916.

electric current to exist even for the normal effect, that for sodium for instance occurring at 227 $\mu\mu$. The photoelectric activity of metals is evidently a complicated phenomenon. Investigation of the optical properties of metals for wave-lengths covering these " normal " maxima would also be of interest.

Preparation of the Mirrors, and Means of Support.

The metal surfaces used were of two kinds: those of the solid metal in a lump against quartz, such as had been used by R. W. and R. C. Duncan and by Nathanson; and thin films of the metal deposited on quartz by evaporation at the temperature of liquid air. The arrangement for making mirrors of the first kind is shown in Fig. 2. Pieces of

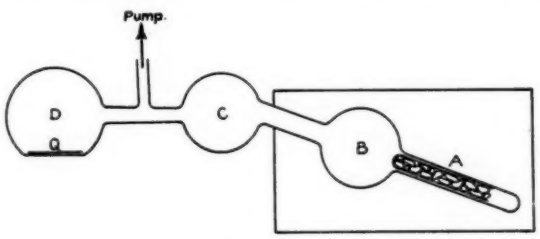

Fig. 2.

sodium or potassium are placed in a small tube and slipped into the end A, which is then sealed off. The apparatus is heated locally with a Bunsen flame to drive off water vapor and gases, particularly from the plate Q which is of fused quartz. Crystalline quartz is very likely to crack when the hot metal is poured over. The pump is kept in action until the pressure has become fairly low and perfectly steady. Parts A and B are now placed inside a can and heated slowly, and the gas evolved is pumped off. In time the metal distils over into C, where it collects in a small pool. After the apparatus is sealed off from the pump the molten metal is poured over into D and brought into contact with the quartz plate. If the cooling of the metal takes place slowly and uniformly, and if the quartz is clean, the metal shows little tendency to withdraw from the quartz surface and the resulting mirror presents a fairly large area free from blemishes. Mirrors that are dotted over with small holes result from too rapid or non-uniform cooling. Bulb D is cracked open, the quartz plate with the metal adhering to it is removed, and " half and half " is quickly applied until the metal is made air-tight. Mirrors of sodium and potassium made in this way kept very well during many weeks, apparently without any deterioration. During the damp days of spring the metals showed a tendency to oxidize around the edges, hence special precautions are necessary to preserve them.

For purposes of support, a glass plate is sealed on parallel with Q. The mirror is supported vertically (see Fig. 3) against a brass plate, held rigidly, in which had been drilled a hole 5 mm. in diameter.

The mirror was pressed against three pins in the brass plate, by a tight spring surrounding a brass rod that touched the glass plate. With this arrangement the mirrors could be replaced with great accuracy in the same position relative to the hole, which was very essential for

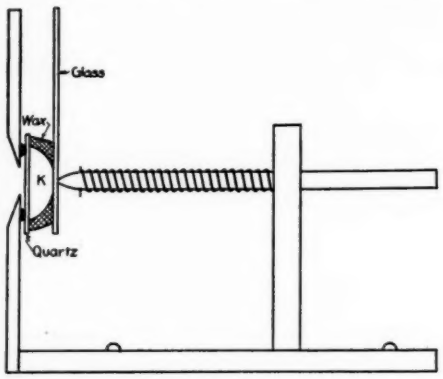

Fig. 3.

readings that could be reproduced. The front side of the brass support was blackened with soot. The light was incident on the mirror at an angle of 10°.

The making of metallic films of sodium and potassium by cooling the glass or quartz surface to the temperature of liquid air was suggested by Prof. R. W. Wood.[1] A small amount of metal is distilled over on to the surface of a bulb, similarly to the method already described (see Fig. 2), except that A is heated locally, driving the metal to B, and is then sealed off from the apparatus. B is then heated sending the metal to C, and is also sealed off. Two distillations are usually sufficient. The quartz plate is now placed in C. The apparatus is now removed from the pump, and bulb D, of various shapes and sizes according to the nature of the experiment, is cooled down to $-$ 190° C, as is also the lower part of C, containing Q. A small flame is then applied to the upper part of C, thus vaporizing the metal, some of which deposits on the cold quartz plate below. When conditions are favorable the resulting film has a truly metallic appearance, quite different from the colloidal film formed at ordinary temperatures. On warming up to room temperature, a thin film becomes peppered with holes and appears to evaporate; an opaque film loses its luster.

[1] R. W. Wood, Philosophical Magazine, 38, 98, 1919.

Measurement of Intensity.

As in Hulburt's[1] and in Nathanson's[3] work, the intensity of the reflected light was measured directly by means of a photoelectric cell. This was a bulb coated with sodium, with a short tube about 1 cm. in diameter carrying a fluorite window. This cell, which was used by Dr. E. O. Hulburt, in his research on reflecting power of metals, obeys the law of direct proportionality between the light intensity and the photoelectric current, through a range of intensities far exceeding those used in the present work. This was tested by varying the distance between the cell and a tungsten lamp. A later test for monochromatic light (4358 Å. and 3130 Å.) gave the same result. Except at the anode and window the cell was covered with tinfoil, which served very well to remove charges from the surface of the glass. It was found advisable to keep the cell in a box in order to make the "dark leak" small. The anode, which was connected to a sensitive electroscope, was charged to 110 volts; the cathode and case of electroscope were earthed. In the winter the dark leak took 20 to 30 minutes, while many of the actual readings for the intensity of the reflected light occupied 10 to 20 seconds. In the spring the dark leak was greater. It is measured by taking the rate of motion of the gold leaf when the mirror is removed from the brass support (see Fig. 4 below).

Normal Incidence.

Arrangement of Apparatus.—This is shown in the following diagram. The apparatus was set up in a dark room, and suitable screens were used to protect the mirror M from all light except that passing through S_2. The source of light was a mercury arc in quartz, designed by Dr. A. H.

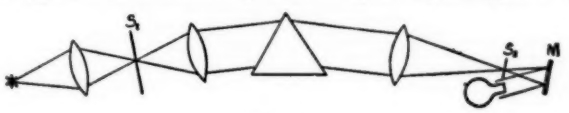

Fig. 4.

Pfund, and run on storage batteries at 120 volts. This lamp runs very steadily for hours, giving light of constant intensity. The light is passed through a quartz spectrograph so designed (by Dr. Pfund[2]) that the different wave-lengths were brought into focus at the slit by a single rack and pinion adjustment. The first slit (towards the arc) was 1 mm. in width, the second slit was .6 mm.; these were kept the same throughout. The intensities of the lines in the arc differ greatly. The more intense lines were cut down by the use of suitable screens in front of S_1; narrowing S_1 failed to give reproducible results.

[1] Hulburt, Astrophysical Journal, 42, 205, 1915.

[2] Pfund, Physical Review, 7, 29, 1916.

Since the reflecting power of mercury against quartz has been determined with accuracy by Hulburt[1] in the ultra-violet, using a direct method with a photoelectric cell, and by Meier[2] in the visible spectrum and partly in the ultra-violet using the katoptric method, a comparison method with mercury was decided upon for the present investigation. The procedure is to place the mirrors in succession—say mercury, sodium, potassium, mercury—in the brass support at M, reading for each the rate of fall of the gold leaf. The second setting of the mercury mirror serves as a check on the constancy of the incident light. The readings obtained for a given set of mirrors for different sets of observations differed by not more than 6 per cent.

COMPUTATION[13] AND RESULTS.

If r is the reflecting power of quartz,

R_q is the reflecting power of sodium or potassium in contact with quartz,

R' is the reflecting power of the whole mercury mirror,

i is the photoelectric current due to the light reflected by the whole sodium or potassium mirror,

i' is the photoelectric current due to the light reflected by the whole mercury mirror,

then, to a fair approximation,

$$R_q = \frac{\frac{i}{i'} R' - r}{(1 - r)^2}.$$

The value of r is computed from Fresnel's formula $\left(\frac{n-1}{n+1}\right)^2$; the appropriate values of n, the refractive index of quartz, are interpolated from those determined by Martens.[15] The values of i and i' are inversely proportional to the rate of leak of the electroscope (corrected when necessary for the dark leak).

Some of the results are shown in Table I., where i_{Na}/i'_{Hg} is the ratio of the intensities of the reflected light from the whole sodium mirror and the whole mercury mirror respectively. The number of seconds given in parentheses is the original reading, not corrected for the dark leak. The corrected reading is the one directly below. R_q is the reflecting power of the metal in contact with quartz. The reflecting power of the metal alone, found by Ingersoll's[4] method, is only a few per cent.

[1] Hulburt, Astrophysical Journal, 46, 1, 1917.

[2] Meier, Annalen der Physik, 31, 1017, 1910.

[3] Martens, Annalen der Physik, 6, 603, 1911.

[4] Ingersoll, PHYSICAL REVIEW, 29, 392, 1903.

higher. The results given here are not of sufficient accuracy to warrant its use. R_q' is the value R_q (for potassium) assumes when multiplied by a suitable factor. This factor is obtained by comparing the value of R_q for λ 5461 Å. with that given by Nathanson[3] for normal incidence.

The graphs shown in Fig. 5 represent the average values of R_q for the two metals taken from many sets of observations. It is interesting

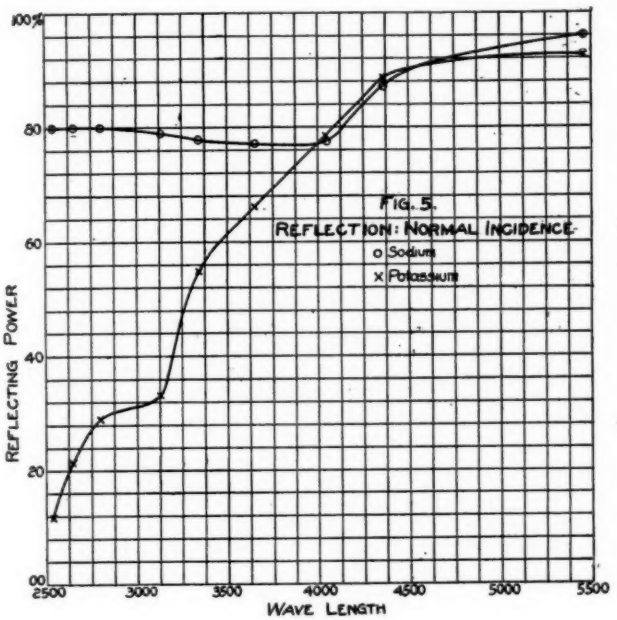

Fig. 5.

that the reflecting power of sodium shows a minimum in the region in which the maximum of the selective effect occurs. Although the angle of incidence was small, the electric vector had a small component perpendicular to the surface of the mirror. Since a greater energy of emission in the form of electrons suggests a greater absorption of light for this wave-length, a diminution in the reflecting power of sodium might be expected. A second point worthy of notice is the high reflecting power of sodium in the ultra-violet—nearly 80 per cent.; this is higher than for any other substance that has been investigated.

The curve for potassium on the other hand shows a rapid decrease in the reflecting power with wave-length, the decrease setting in rapidly below 4358 Å. the wave-length at which the maximum of the selective effect for potassium occurs. The abrupt decrease at 3130 Å. and slight decrease at 2804 Å. may possibly mean that a maximum photoelectric current for the normal effect is to be expected in the vicinity of 3130 Å.

TABLE I.

Wave-length.	Reflection from Sodium. No. of Seconds. Hg.	Na.	$\frac{i_{Na}}{i'_{Hg}}$.	R'.	R_q.	Reflection from Potassium. No. of Seconds. Hg.	K.	$\frac{i_K}{i'_{Hg}}$.	R_q.	R'_q.
5461	21.2	15.2	1.40	66	96.0	21.2	19.4	1.10	73.4	92.5
	21.4	15.2				21.4	19.4			
	(35.6)	(26.0)	1.39			(35.6)	(33.7)	1.06		
	37.1	26.8				37.1	35.1			
4358	14.2	10.6	1.35	62	87.5	14.2	12.6	1.12	69.7	88.0
	13.8	10.2				13.8	12.4			
	13.0	9.5	1.37			13.0	12.0	1.08		
4047	14.2	10.5	1.35	57	80.5	14.2	12.9	1.10	62.7	79.0
	13.2	9.6	1.38			13.2	12.3	1.07		
3650	20.2	14.0	1.40	55	78.5	20.2	18.6	1.08	59.5	74.0
	20.4	14.8				20.4	18.8			
	15.4	11.2	1.37			15.4	14.4	1.06		
	14.8	10.8				14.8	14.2			
	15.2					15.2				
3341	13.8	10.0	1.38	55	78.0	13.8	16.0	.86	46.0	58.0
	13.6	9.8				13.6	16.0			
	15.2	10.6	1.37			15.2	18.0	.84		
	15.0	11.0				15.0	18.0			
		11.0								
3130	22.0	16.0	1.38	55	78.0	(22.0 22.0)	(40.2 39.8)	.54	26.4	33.2
	22.0	15.8				22.6	41.7			
	18.0	12.8	1.40			(18.0 17.8)	(34.4 34.4)	.51		
	17.8	12.8				18.2	35.8			
2804	(173)	(127)	1.44	55	80.0	(173)	(318)	.43	20.0	25.2
	215	149				215	503			
	(324)	(273)	1.36			(324)	(466)	.40		
	629	464				629	550			
2653	(173)	(129)	1.43	55	81.0	(173)	(388)	.32	14.0	17.6
	215	150				215	675			
	(167)	(124)	1.42			(167)	(369)	.33		
	204	144				204	622			
2536	(63.2 64.0)	(47.2 46.8)	1.38	55	78.0	(63.2 64.0)	(213 213)	.25	8.4	10.6
	68.5	49.5				68.5	278			
	(65.0 64.4)	(48.6 49.0)	1.35			(65.0 64.4)	(231)	.22		
	69.5	51.5				69.5	309			

However, line 2804 A. has a very low intensity and perhaps not much importance can be attached to this value.

A second set of sodium and potassium mirrors backed by the same quartz plates gave similar curves with the exception of the minimum of sodium, which occurs slightly farther towards the short wave-lengths.

No other change was made in the apparatus except for the hole in the brass support, which was enlarged to 8 mm.

Oblique Incidence: Polarized Light.

A Rochon prism, one part of which was quartz and the other part calcite, cemented with glycerine, was used as polarizer. In the path of the light from S_2 was placed a quartz lens, following this the Rochon prism, finally the mirror at the focus of the lens in such a position as to receive only one image. The angle of incidence used was 45°. Since the quartz plates backing the metals are fused, and nothing is interposed between the Rochon prism and the mirror, the state of polarization of the light is known as the metal-quartz surface. The ordinary ray was used, with the electric vector either in the plane of incidence or perpendicular to it, effected by turning the prism through 90°. The extraordinary ray fell beyond the mirror on the soot-blackened surface of the brass support. The intensity of the ordinary ray when polarized so that the electric vector is in the plane of incidence was not the same as when it was polarized so that the electric vector is perpendicular to the plane of incidence, except for two of the lines used. The ratio of the two was found by removing the brass support and placing the photoelectric cell in the direct beam of light. Two methods were used (see Fig. 6); that

Fig. 6.

of focussing the light just within the window of the cell, so that the cell receives practically the whole beam of light; and that of placing the window of the cell in the diverging beam so that the central part of the image is on the window. The two methods agreed within 5 per cent., which is as accurate as could be expected. Because of deficiencies of the Rochon prism, the image shifts sidewise and downward when the prism is turned; the mirror (8 mm. diameter) is sufficiently large to accommodate this shift, but the reflected image travels away from the window of the cell. Hence it became necessary to adjust the cell for each adjustment of the Rochon prism. Lines 3341 Å. and 3130 Å. lose greatly in intensity on passage through the prism; hence the difficulty of setting the cell accurately for the reflected images of these lines became very great. A large number of observations have been made, but not much accuracy can be claimed for the values obtained. An error of 10 per cent. or even more is highly probable.

The wave-lengths below 3130 Å. were absorbed by the prism.

Whether the cell is used for the direct beam or the reflected beam, the direction of the electric vector relative to the sodium surface of the cell remains the same, because of the spherical shape of the cell.

The ratio of the intensities of the reflected beams $E_{\|}/E_{\perp}$ was investigated as a function of the wave-length. The sodium or potassium mirror having been adjusted in the brass support and the spectrograph set for a given wave-length, the rate of leak of the electroscope was found for each component. This ratio, when plotted against the wave-lengths, should yield the information desired in relation to the photoelectric effect, if any marked change in the reflection occurs: that is, such a curve would correspond to the $E_{\|}/E_{\perp}$-photoelectric current curve referred to on page 2?

Some of the data are shown in Table II. The first numbers in the seventh column are obtained by taking the inverse ratio of the rates of leak in columns two and three; and similarly for the eighth, fourth and fifth columns.

TABLE II.

Wave Length.	Polarized Light. Angle of Incidence 45°.						
	Time in Seconds.				Ratio of Intensities $E_{\|}/E_{\perp}$.		
	Na.		K.		Incident Light.	Reflected Light Na.	Reflected Light K.
	$E_{\|}$.	$E_{\perp}$.	$E_{\|}$.	$E_{\perp}$.			
5461	29	24	17.0	12.6	.91	.83 ÷ .91 = .91	.74 ÷ .91 = .81
	30	25	17.2	12.6			
4358	10.6	9.6	21.6	17	.93	.90 ÷ .93 = .97	.79 ÷ .93 = .85
	10.8	9.6					
4047	9.6	8.8	27	24	1.03	.92 ÷ 1.03 = .89	.9 ÷ 1.03 = .88
	9.8	9.0	26	24			
3650	7.6	9.2	18	19.4	1.0	1.21 ÷ 1 = 1.21	1.09 ÷ 1 = 1.09
			17.8	19.6			
3341	(49)	(38)	29.8	23			
	(50)	(37)	30	23.6	1.0	.73 ÷ 1 = .73	.78 ÷ 1 = .78
	56	41					
3130	17	14.2	15	10	.77	.82 ÷ .77 = 1.06	.68 ÷ .77 = .88
	17.2	14	14.6	10			

The graphs of Fig. 7 represent the average of a number of observations. The maximum in the neighborhood of 3650 Å., common to both metals, is rather striking, but undoubtedly is due to the metals and not the quartz, the reflection of which for unpolarized light is less than 6 per cent. at 45°. It cannot be due to a " selective effect " from the cathode of the cell, for the reason given above. The minimum for sodium in the neighborhood of 3341 Å. together with the maximum at 3650 Å. shows a

decided change in the reflecting power for the two beams polarized at right angles, through the range of wave-lengths in which the maximum of the selective effect occurs. When the electric vector is so directed that it has a component perpendicular to the illuminated surface of the metal, it appears that at the critical wave-length of the selective effect less light energy is reflected by the metal, hence more is absorbed. This

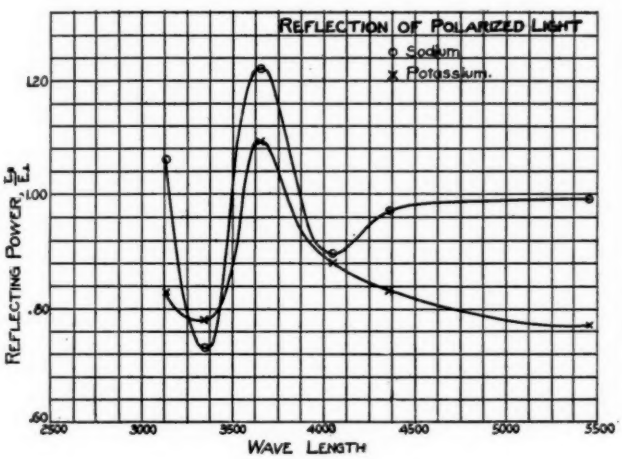

Fig. 7.

is not what might have been expected from the usual point of view, that the selective effect is due to a large absorption of energy near the surface—that is, the extinction coefficient becomes large, from which a higher reflecting power is expected. According to Nathanson's data the ratio $E_{\parallel}/E_{\perp}$ is less than unity in the visible spectrum for 45° incidence, although his value for potassium is considerably higher than the one given here.

Potassium again fails to show any marked deviation at 4358 Å., but this may possibly be due to the absence of data in the interval 4358–5461 Å. Without this corresponding minimum for potassium it is hardly possible to draw any conclusions as to whether there is or is not a direct connection between the reflecting powers of the metals and the selective effect. This work must be regarded only as a preliminary attempt.

FILMS DEPOSITED AT LOW TEMPERATURES.

An attempt has also been made to get the reflecting power of potassium, and the transmitting power of potassium and sodium, using films of the metals deposited on quartz plates and glass plates at low temperatures. The apparatus for the reflection is represented in Fig. 8. Bulb *A* is

coated with potassium which has been distilled over from tubes similar to those shown in Fig. 2. In the bottom of this bulb is a piece of glass half of which is plated with nickel (deposited by cathode sputtering). This half is covered by a piece of metal C which rests on M, but can readily be shaken off. On the lower side of M is attached a piece of iron, by means of which M can be manipulated with a magnet. In the bulb B is a piece of brass with a groove in which M can slide back and forth. Q is a quartz window. The lower half of B and the lower part of A are placed in vessels containing liquid air. When sufficient time

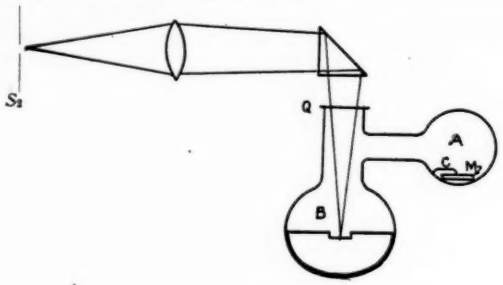

Fig. 8.

has elapsed to allow the cooling to take place, by means of a small flame the potassium is driven down from the top of A on to the uncovered part of M. Opaque films only were used. M is now brought quickly over into B, which is kept in liquid air throughout this experiment.

The light from S_2 (see Fig. 8) was passed through a quartz lens, then by means of a right-angled quartz prism was directed downward, almost vertically, through Q on to M, which is now in the groove in B. By means of a magnet the nickel surface and the potassium surface were in turn brought into the center of the groove, and reflected back the light through Q, into the photoelectric cell. In this case nickel served as the comparison mirror. The values of the reflecting power of nickel are taken from those given by Hagen and Rubens[1] in the visible spectrum, and by Hulburt[11] in the ultra-violet spectrum. The reflecting powers of the two metals are approximately inversely proportional to the rates of leak of the electroscope. Due to the presence of gases or impurities on the glass M these mirrors were somewhat cloudy. The reflection curves in general follow the one shown for potassium in Fig. 5, but the values are somewhat low.

For the transmitting power, a form of apparatus such as is shown in Fig. 9 was used. A glass tube with two quartz windows Q_1, Q_2 contained a metal partition P with a hole H. The part of the tube at P was kept

[1] Hagen and Rubens, Annalen der Physik, 1, 352, 1900.

cold by means of cotton batting soaked with liquid air. Part of bulb A, containing the quartz plate Q, was cooled in liquid air, and as before the potassium was driven on to Q by heating A gently with a small flame. (Bulb B contains the sodium.) Q was then brought quickly into the main tube up against P so that H was completely covered. The tube

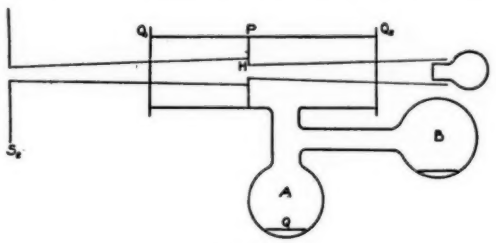

Fig. 9.

was so supported that it could readily be moved into the beam of light or out of it. Thus the cell received in turn the transmitted beam and the direct beam. It is also a simple matter to remove the film of metal from Q and to measure the loss of intensity of the incident light due to

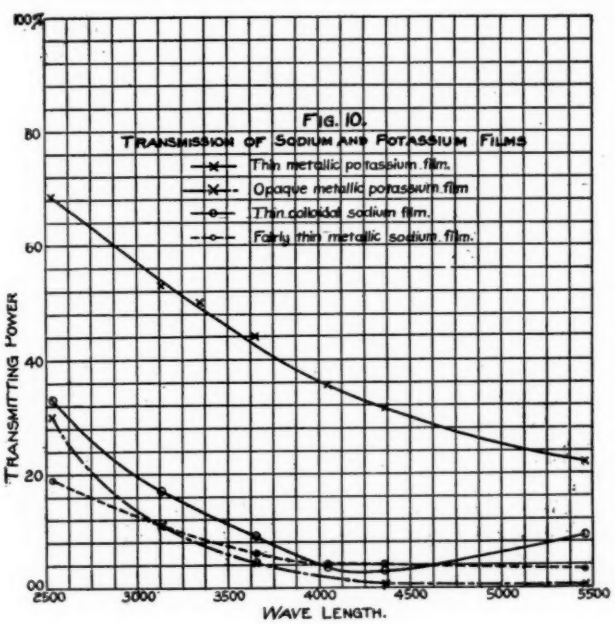

Fig. 10.

Q_1, Q_2 and Q; and by removing Q the loss of intensity due to Q_1 and Q_2. The transmitting power of the film is then readily computed.

The results are shown for a few films in the graphs of Fig. 10. The

divergence of the curves for the metallic and colloidal films is noticeable, particularly in the visible region. The most striking fact is the greater transmitting power of potassium.

SUMMARY.

1. The reflecting powers of sodium and potassium surfaces backed by quartz have been determined directly for normal incidence (10°), as a function of the wave-length, for the range of wave-lengths 5461 Å.–2536 Å. Sodium is the best reflector known in the ultra-violet region, giving 80 per cent. at 2536 Å.; potassium is the worst reflector in the ultra-violet, giving 11 per cent. at 2536 Å. In the case of sodium, there is evidence of a flat minimum in the neighborhood of 3300 Å–3600 Å.

2. The reflecting power of these surfaces for polarized light has been measured in the region 5461 Å.–3130 Å. by a determination of the ratio $E_{\parallel}/E_{\perp}$ as a function of the wave-length ($E_{\parallel}$ is the intensity of the reflected light when the electric vector of the incident light is parallel to the plane of incidence, $E_{\perp}$ the intensity of the reflected light when the electri-vector of the incident light is perpendicular to the plane of incidence); Both metals show a maximum value of this ratio in the vicinity of 3650 Å.. sodium shows a decided minimum in the vicinity of 3341 Å.

3. Metallic films of the two metals have been deposited at low temperac tures, and the reflecting and transmitting powers of these films examined. This promises to be a fruitful field of research, as the photoelectric current and optical properties can be examined as a function of the thickness of the film.

The transmitting power of potassium is decidedly higher than that of sodium.

It gives me great pleasure to express my gratitude to Professor Ames for his interest throughout the course of this work, and to Professor Pfund, who proposed the problems taken up, and whose assistance and helpful suggestions have made the execution of the work possible.

BIOGRAPHICAL NOTE.

Mabel Katherine Frehafer, daughter of Charles Milton Frehafer and Caroline (Ball) Frehafer, was born in Philadelphia on July 7, 1886. Her early training was received in Philadelphia. In 1904 she entered Bryn Mawr College, and in 1908 received the degree of Bachelor of Arts. She held a scholarship at Bryn Mawr from the City of Philadelphia for the years 1904–8. During the year 1908–9 she was a graduate student in physics and mathematics at the University of Wisconsin, and in 1909 received the degree of Master of Arts. She was appointed fellow in

physics at Bryn Mawr College for the year 1909–10. From 1910–14 she was demonstrator in physics at Bryn Mawr College. She was enrolled as a student of physics and mathematics in the summer school of Wisconsin in 1914. During the year 1914–15 she was half time assistant and student at the University of Wisconsin. For the first semester of 1915–16 she was full time assistant at Wisconsin, and for the second semester teacher of physics in the Germantown High School for girls, Philadelphia. For two years beginning 1916 she was instructor in physics at Mt. Holyoke College. She entered Johns Hopkins University as a graduate student in October, 1918, making physics the principal subject, mathematics the first subordinate, and chemistry the second subordinate. She attended courses in physics and mathematics given by Professor Ames and Dr. Murnaghan.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE CHICAGO MEETING, NOVEMBER 28 AND 29, 1919.

THE 100th regular meeting of the American Physical Society was held in the Ryerson Physical Laboratory of the University of Chicago on Friday and Saturday, November 28 and 29, 1919. The attendance was unusually large and this was especially true of members from the eastern portion of the country; the average attendance was about one hundred and sixty with a maximum of over two hundred on Saturday morning.

There was a short business session on Saturday morning, November 29, 1919, at which an amendment to the By-Laws, as recommended by the Council, was unanimously adopted. The amendment refers to Artical I—Dues, Section 1; as amended the Section reads: The annual dues of regular members shall be ten dollars and of associate members eight dollars, payable on the 1st of January.

A beautiful wreath of laurel in memory of Professor Wallace C. Sabine, who was vice-president of the Society at the time of his death on January 10, 1919, was presented to the Society by Colonel George Fabyan of Geneva, Ill. It was a token of esteem and appreciation especially appropriate at this hundredth meeting.

At a regular meeting of the Council, held on November 28, 1919, the following elections were made: *elected to regular membership*, Dugald C. Jackson, Charles B. Bazzoni; *elected to associate membership*, Lewis G. Abernathy, E. S. Akeley, C. N. Anderson, Mary Ruggles Andrews, I. G. Barber, H. Louisa Billings, Christian F. Boeck, Ira S. Bowen, H. B. Briggs, M. C. Bubenzer, Chas. W. Chapman, Allison A. Clokey, B. L. Conley, Aurelius L. Corcuera, Charles B. Crofutt, Edith E. Cummings, Margaret K. Dawson, Ralph D. Doner, Charles H. Dwight, H. E. Farnsworth, Floyd A. Fireston, E. V. Floyd, Floyd Hill Frame, M. L. Frazier, H. A. Frederick, E. C. Fritts, Jr., Roscoe H. Gerke, L. H. Gilmore, John C. Hamilton, George R. Harrison, T. R. Harrison, Kenneth Hartley, D. L. Hay, L. A. Hazeltine, Ann Hepburn, George W. Horton, J. Warren Horton, James D. Jordan, Earl C. Karker, Lewis R. Koller, A. Collins Ladner, Thomas J. Love, Isreal Maizlish, Sister Aloysius Marie, Edward J. Martin, Robert C. Mathes, L. L. Nettleton, Robert F. Paton, E. B. Penrod, Eugene Peterson, A. D. Power, R. L. Price, Phil P. Quale, Charles W.

Robbins, Irwin Roman, E. Frances Seiler, H. H. Sheldon, R. C. Siegel, L. B. Slichter, William R. Smythe, Howard C. Stearns, John C. Steinberg, R. R. Stephenson, John Q. Stewart, Ting Supao, Joseph W. Tanch, E. G. Taylor, H. C. Terry, John X. Thompson, Earl W. Thomson, Lewi Tonks, Forrest G. Tucker, Elmer N. Turnquist, Frederick P. Upton, Clarence W. Wallace, John C. Warner, G. B. Watson, Warren Weaver, Hugh E. Weightman, H. T. Wenzel, Richard M. White, W. T. Whitney, Clodius H. Willis; *transferred from associate to regular membership*, A. G. McGougan, Wheeler P. Davey, Kasson S. Gibson.

The centenary occasion was marked by a symposium of eight papers of unusual importance on the Electron-Tube, presented by invitation of the President of the Society. The program of the Symposium was as follows:

Phenomena in Pure-Tungsten Filament Electron Tubes. IRVING LANGMUIR.

Phenomena in Oxide-Coated Electron Tubes. H. D. ARNOLD.

The Relations of the Constants of an Electron Tube to its Physical Dimensions. L. A. HAZELTINE.

Theory of Action of Electron Tubes as Amplifiers. JOHN M. MILLER.

Theory of Action of Electron Tubes as Generators. JOHN H. MORECROFT.

High Power Transmission Sets. W. C. WHITE.

Electron Tubes in Telephony. O. B. BLACKWELL.

A Method of Receiving Very Short Waves. E. H. ARMSTRONG.

The ordinary program contained thirty-two papers, six of which were read by title, the program was as follows:

The Change of Molecular Kinetic Energy into Molecular Potential Energy—The Entropy Principle. WILLIAM D. HARKINS and L. E. ROBERTS.

The Spectro-Photo-Electric Sensitivity of Thaloside. W. W. COBLENTZ. (Read by title.)

Duration of the Light Emission from a Radiating Hydrogen Atom. A. J. DEMPSTER.

The Fine Structure of the Near Infra-Red Absorption Bands of the Halogen Acids. ELMER S. IMES and H. M. RANDALL.

Vibrational Frequencies of the Halogen Acid Molecules. W. F. COLBY.

The Nuclei of Atoms and the New Periodic System. W. D. HARKINS.

Symmetrical Subdivision of Anode Glow in Helium Discharge Tubes. G. M. J. MACKAY.

The Spectral Distribution of the Radiant Energy of Metals. GROVER R. GREENSLADE.

The Construction of Three-Element Power Electron Tubes. EARL M. TERRY and C. M. JANSKY, JR.

The Nature of the Process of Ionization by Alpha Particles. R. A. MILLIKAN, V. H. GOTTSCHALK, and M. J. KELLY.

Threshold Phenomena and the Law of Radiation. JAKOB KUNZ.

The Ionization Potential of Mercury Vapor as a Function of the Temperature of the Cathode. T. C. HEBB. (Read by title.)

On Ionization by Successive Impact, and Its Action in Low Voltage Arcs. KARL T. COMPTON.

Radiation and Ionization Produced in Helium by 20-volt Impacts. KARL T. COMPTON.

Ionization Potentials of Argon, Nitrogen, Carbon Monoxide, Helium, Hydrogen and Mercury and Iodine Vapors. CLIFTON G. FOUND.

Studies with the Ionization Gage. I. Construction and Method of Calibration. S. DUSHMAN and C. G. FOUND.

Studies with the Ionization Gage. II. Relation between Ionization Current at Constant Pressure and Number of Electrons per Molecule of Gas. S. DUSHMAN and C. G. FOUND.

Charcoal Activation. H. H. SHELDON.

The Absorption of Air by Charcoal at Reduced Pressures near Liquid Air Temperature. THOS. E. DOUBT, HARRY C. THOMPSON, and H. H. SHELDON.

An Apparent Compression by Adsorption. W. D. HARKINS and D. T. EWING.

Experiments on Osmotic-Electric Electromotive Forces. A. P. CARMAN and E. C. FRITTS, JR. (Read by title.)

Neutral Magnetization. A. W. SMITH and H. E. HAMMOND.

The Rigidity of the Earth. A. A. MICHELSON and HENRY G. GALE.

Possible Standard of Sound—Energy of, etc. CHAS. T. KNIPP.

Stroboscopic Formulae used by Poske, by Michelson, and by Reed, Respectively, for Rating Tuning Forks, as Special Cases of the More General Stroboscopic Equation. L. E. DODD. (Read by title.)

Note on the Theory of Longitudinal Vibrations in Rods Having Internal Losses. W. G. CADY.

The Functions of Intensity and Phase in the Binaural Location of Pure Tones. G. W. STEWART.

The Viscosity-Temperature Curves of Seven Varieties of Optical Glass. E. W. WASHBURN and G. R. SHELDON. (Read by title.)

The Measurement of Very Short Time Intervals. PAUL E. KLOPSTEG. (Read by title.)

The Effective Capacity and Resistance of a Condenser for High Frequency Currents. F. C. BLAKE.

The Dielectric Constant of Kerosene and Water for High Frequency Currents. F. C. BLAKE and CHARLES SHEARD.

The Electric Field of a Rotating Magnetic Doublet. W. F. G. SWANN.

DAYTON C. MILLER,
Secretary.

Threshold Phenomena and the Law of Radiation.[1]

By Jakob Kunz.

If a beam of monochromatic light falls upon a metal, it will in general not produce photoelectric effect until the frequency reaches a critical value given by the equation $(n - n_0)h = eV = \frac{1}{2}mv^2$. There is a threshold in the frequencies of the light, characteristic for each metal, but always expressed by the first equation. This holds for visible, ultra-violet and x-ray light. In the opposite effect, when moving electrons collide with atoms or molecules in the vapour state, then critical or threshold velocities are observed which are determined by the same equation. In a given vapor for instance of alkali metals, in general two thresholds are observed: a resonance and an ionization potential. For a certain lower value the velocity of the electrons is just sufficient to produce radiation of the first line of the principle series of alkali metals. For a higher critical value of the velocity, the electrons split the above in two parts and ionization takes place for a velocity determined by the equation:

$$\frac{1}{2}mv^2 = eV = hn,$$

where n corresponds now to the convergence frequency of the principal series. Similar relations have been found in the alkali earth group, in magnesium, zinc, cadmium, mercury thallium, etc. In mercury vapor, for instance, there is a first resonance potential at 4.9 volts, a second at 6.7 and an ionization potential without radiation at 10.4 volts. Hydrogen seems to have three thresholds: the first at 11 volts: ionization with radiation the second at 13.6 volts, radiation with an increase of ionization, and the third at 15.8 volts where a new ionization sets in without increase of radiation.

When electrons in a Röntgen tube strike a metal, they produce x-rays in general of two kinds: a general or pulse radiation and characteristic rays. It has recently been found that for the general radiation all frequencies occur up to a certain limiting value given by the equation $\frac{1}{2}mv^2 = eV = hn$, and the same relation holds for the characteristic rays.

Thresholds seem to appear generally when light energy is transformed in kinetic energy of electrons or where kinetic energy of electrons is transformed into light energy or used up for ionization.

At least three different attempts can be made at an explanation of these thresholds. It might be due to a special property of the ether, or due to a property of the electron, or due to the atoms from which the electrons are set free. We shall make this latter assumption and imagine that in a given substance especially in a solid state we find thermal energy of agitation and intrinsic elecromagnetic energy stored up in the atoms or molecules; then we can deduce from the canonical distribution of systems of Gibbs the fundamental law of radiation if we make the following assumptions: (1) For every degree of freedom there is a threshold in this intrinsic electromagnetic energy; (2) the entropy

[1] Abstract of a paper presented at the Chicago meeting of the American Physical Society, November 28, 1919.

corresponding to the intrinsic energy for high temperature $Li = 3Nk \log E_0/n$ is a universal constant. $E_0/n = h$; (3) free energy of thermal energy alone is used for the calculation of the entropy of the oscillators. The thermal energy of the oscillators appears then in the form:

$$M = 3N \frac{hn}{e^{\frac{hn}{kT}} - 1}$$

which leads directly to Planck's law of radiation.

THE IONIZATION POTENTIAL OF MERCURY VAPOR AS A FUNCTION OF THE TEMPERATURE OF THE CATHODE.[1]

BY T. C. HEBB.

IN two previous papers I have shown that mercury vapor can be ionized with a potential difference as low as 4.9 volts. From these results it was concluded that this potential difference was characteristic of mercury vapor. This conclusion was natural in view of the quantum relation which appears to hold for 4.9 volts.

I have lately performed some experiments with a new design of apparatus and I find that there is no apparent significance in this value of 4.9 volts. I have found that mercury vapor will ionize at lower voltages, the lowest so far obtained is 3.2 volts. I have also found that there is a linear relation between the striking voltage of an arc—the ionization potential—and the temperature of the cathode. This relation, which appears to be represented by the equation $V = 10.5 - .002T$, where V is the striking voltage, 10.5 is the ionization potential of mercury vapor and T is the absolute temperature of the cathode, holds only for the higher temperatures of the cathode.

The experiments will be published at an early date.

UNIVERSITY OF BRITISH COLUMBIA,
VANCOUVER, B. C.

ON IONIZATION BY SUCCESSIVE IMPACT, AND ITS ACTION IN LOW VOLTAGE ARCS.[1]

BY KARL T. COMPTON.

THE ionization of a vapor, or the production of its many-lined spectrum, at voltages distinctly below its minimum ionizing potential has been variously accounted for by the photoelectric action of excited radiation on the vapor or on the cathode, by electron impacts in quick succession on some of the molecules, or by the joint action of radiant energy and energy of impact. Increased electron emission from the cathode due to its bombardment by

[1] Abstract of a paper presented at the Chicago meeting of the American Physical Society, November 28, 1919.

positive ions may aid in sustaining an arc but cannot be a primary factor in causing it to strike. There is experimental evidence against the hypothesis of photoelectric action on the vapor. Photoelectric action on the cathode occurs, but is shown to be insufficient to account for the observed ionization. Recent work by Stark gives information regarding the order of magnitude of the interval of time during which a molecule may retain energy from an impact, and thus makes possible a quantitative estimate of the magnitude of the effect due to successive impacts.

Assuming that ionization may be produced if a molecule is struck by an electron with velocity greater than the minimum radiating velocity followed by another similar impact within the time interval τ determined by Stark, it is shown that the fraction of the collisions which result in ionization is approximately $nNf\tau/N^1$ if the ineffective collisions are inelastic and is $4r^2UpN^2$-$nf\tau/XN^1$ if ineffective collisions are elastic. Here p is the gas pressure, n is the number of bombarding electrons crossing unit area per second, X is the electric intensity, f is the probability of producing radiation at an impact with velocity equivalent to U volts and the remaining quantities are constants. Substitution of experimental values shows that the effects of successive impact are entirely negligible in the case of the inelastic gases, but that in mercury vapor under the most favorable conditions tested about 0.0002 of the impacts follow others in sufficiently close succession to produce ionization by successive impacts.

An extension of the analysis leads to the conclusion that the intensity of visible (arc) radiation at voltages below the ionizing potential is $R = KU^3(U - V_0)^2p^5n^3/X^3$, which is in general accord with the observed influence of pressure, applied field and current density. The effect of positive ions thus produced on the total current, due to the modification of the space charge and to bombardment of the cathode, is considered.

The conclusion is reached that successive impact is an important factor in producing ionization at abnormally low voltages and in causing an arc to strike, but that it alone is insufficient to account for all the observed phenomena.

RADIATION AND IONIZATION PRODUCED IN HELIUM BY 20-VOLT IMPACTS.[1]

BY KARL T. COMPTON.

A SIMPLE and convenient device for distinguishing between ionization and radiation in a gas and for determining the proportion of the effect due to each when both are present is used to examine the effect produced in helium when the atoms are bombarded by electrons which have fallen through 20 volts. Theories of radiation and atomic structure lead to the expectation of radiation alone at this voltage, and this prediction is confirmed by recent work of Horton and Miss Davies. On the other hand, Franck and Hertz have

[1] Abstract of a paper presented at the Chicago meeting of the American Physical Society, November 28, 1919.

pointed out that some of their results with helium can only be explained by supposing that true ionization occurs at 20 volts. (Their results may also be accounted for by assuming absorption of the radiation by the gas.)

Preliminary tests with the apparatus described have indicated that only ionization is detected if the gas pressure in the apparatus is relatively high, but that radiation is detected in larger and larger proportion as the gas pressure is reduced. Experiments are not yet decisive on the question as to whether the effect approaches one of pure radiation as the gas pressure aproaches zero. The results strongly suggest, however, that the primary effect is radiation, as predicted by theory, and that the ionization is a secondary effect due to the impact of an electron against an atom which at the instant contains energy absorbed from the radiation by neighboring atoms. Various tests of this hypothesis are in progress.

IONIZATION POTENTIALS OF ARGON, NITROGEN, CARBON MONOXIDE, HELIUM, HYDROGEN AND MERCURY AND IODINE VAPORS.[1]

BY CLIFTON G. FOUND.

THE object of this investigation was the determination of the effect of the presence of gas on the volt-ampere characteristics of a two-electrode electron discharge tube and the determination of the voltage at which these gases affected the space charge of the tube, that is, the ionization potential of the gases. The method used was one similar to that employed by Foote and Mohler except that a commutator was used which broke the filament heating circuit while the space current was being measured. By this method, the complication of a voltage drop along the filament was avoided.

Thus the relation

$$i = A(V - V_0)^{3/2},$$

where V_0 is voltage equivalent of the initial velocity of the electrons, holds up to the voltage at which ionization occurs in the gas.

The ionization potential of argon was found to be between 15 and 16 volts and was constant for pressures from 1 to 200 bars. With increase in filament temperature, the apparent ionization potential was lowered, but when compensation was made for the initial velocity of the electrons, the real value was found to coincide with that obtained at lower filament temperature.

The ionization potential of nitrogen was found to be about 16 volts, while that obtained for carbon monoxide was about 13.5 or 14 volts.

Ionization commenced in mercury vapor between 10 and 11 volts.

Helium and hydrogen were also studied. A value of 20.5 volts was obtained for helium, but the purity of the gas was questionable. Hydrogen gave a value of 15 volts, but owing to the rapid clean up of hydrogen by the hot filament, this value is unreliable.

[1] Abstract of a paper presented at the Chicago meeting of the American Physical Society, November 28, 1919.

Iodine vapor was found to be ionized by electrons having an accelerating voltage of 8.5 volts.

RESEARCH LABORATORY,
GENERAL ELECTRIC CO.,
SCHENECTADY, N. Y.

STUDIES WITH THE IONIZATION GAGES. I. CONSTRUCTION AND METHOD OF CALIBRATION.[1]

BY S. DUSHMAN AND C. G. FOUND.

A FORM of ionization gage, consisting of three filaments, has been previously described by O. E. Buckley.[2] This construction was found to be unsuitable, as it did not always give linear relations between ionization current and pressure. The design used by the writers is shown in the attached figure. It consists of two tungsten filaments, each wound in the form of a double spiral and arranged co-axially, and a molybdenum cylinder which is also co-axial with the filaments and external to them. The usual connections of the three electrodes for measurements of low pressures (less than 1 bar) are as follows: The center filament is used as a hot cathode with the other filament at +250 volts with respect to the negative end of the hot filament. The temperature of the cathode is adjusted so that the electron emission is kept constant at a value which is ordinarily 10 or 20 milliamperes. The cylinder is connected through a galvanometer to the negative terminal of a 20-volt battery whose positive terminal is connected to the negative end of the cathode. The galvanometer thus indicates the rate at which positive ions are produced by the electron stream from the cathode.

Argon was used as a gas for calibration, as it does not exhibit any "clean up" effects. For pressures above 0.1 bar and up to about 1.0 bar, a sensitive McLeod gage was used, and within this range the ionization current (for constant electron emission) was found to vary linearly with the pressure ($i = kp$, where i = positive ionization, p = pressure and k is a constant). In order to determine whether this relation holds true at still lower pressure, a "flow" method of calibration was adopted. Two large bulbs are connected by a capillary. One of these is connected to a McLeod gage, while the other is connected to the ionization gage. Special care is taken to exhaust the latter to as high a degree of vacuum as possible, as indicated by the very small ionization current, while the other bulb is filled with argon at 10 to 20 bars. Knowing the resistance to flow of the capillary (Knudsen's formula) and the volume of the exhausted bulb, it is possible to calculate at what rate the pressure should increase in the latter. This is compared with the rate of increase of the ionization current, and thus gives a calibration of the gage at very low pressures. The linear relation was found in this manner, to be valid down to .001 bar, and may therefore be assumed to hold true for even lower pressures.

[1] Abstract of a paper presented at the Chicago meeting of the American Physical Society, November 28, 1919.

[2] Proc. Nat. Acad., 2, 68, 3. 1917.

For many purposes where it is desired to measure pressures above 1 bar in a sealed off device, the ionization gage may also be used with the following modifications. The electron emission is maintained at 0.5 milliamperes, and the anode voltage is lowered to 125. With these connections, the range of pressures can be extended up to about 50 bars and the linear relation is still valid.

RESEARCH LABORATORY,
GENERAL ELECTRIC CO.,
SCHENECTADY, N. Y.

STUDIES WITH THE IONIZATION GAGE. II. RELATION BETWEEN IONIZATION CURRENT AT CONSTANT PRESSURE AND NUMBER OF ELECTRONS PER MOLECULE OF GAS.[1]

BY S. DUSHMAN AND C. G. FOUND.

A CALIBRATION of the gage described above was carried out not only with argon, but also with mercury, nitrogen, and carbon monoxide It was observed that, for the same pressure, the ionization current per unit electron current is proportional to the total number of electrons per molecule as calculated from the atomic numbers of the simple atoms. The following table gives the values of k in the equation $i = kp$ for the different gases, at constant electron emission of 0.5 m.a., and the corresponding values of k/N where N denotes the total number of electrons per molecule.

Gas.	N.	$k \times 10^6$.	$(k/N)10^6$.
A	18	1.74	.097
Hg	80	8.4	.105
N_2	14	1.5	.107
CO	14	1.39	.099

A similar determination with iodine at 0° C. (for which the vapor pressure has been measured by Haber[2] gave $N = 106$ (N for iodine $= 53$). Comparing the vapor pressure measurements of Scheel and Heuse for H_2O with the ionization currents at the corresponding temperature, the results were found to be in good agreement with the calculated value $N = 10$. The measurements with H_2 are in fair accord with the value $N = 2$, but owing to the effect of slight traces of impurities and to the clean-up phenomena exhibited by hydrogen in presence of a tungsten filament accurate measurements are difficult to obtain.

Assuming that the ionization current is a measure of the number of collisions between the thermions and electrons in the molecules of gas, it is possible to calculate the mean free path of an electron in the different gases. This, of course, varies inversely with the total number of electrons per unit volume. For argon at 1 bar and room temperature, L, the mean free path of an electron

[1] Abstract of a paper presented at the Chicago meeting of the American Physical Society, November 28, 1919.

[2] Zeit. f. Elektrochem., 20, 296, 1914.

is calculated in this manner to be above 150 cm. By applying to this result the relation

$$L = 4/\pi n d_e^2$$

where d_e = minimum distance of approach between two electrons for ionization, and n = number of electrons per cm.^{3}, it is found that $d_e = 4.4 \times 10^{-9}$ cm. approximately.

Specially designed gages have been made up for an accurate determination of this constant, and the results of this investigation will be reported in the near future.

RESEARCH LABORATORY,
GENERAL ELECTRIC CO.,
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CHARCOAL ACTIVATION.[1]

BY H. H. SHELDON.

RECENTLY there have been published certain papers dealing with charcoal activation[2] which propose a hydrocarbon hypothesis. The lack of published data either in support of or in contradiction to this theory led the author, on the suggestion of Dr. Harvey B. Lemon, to look for this evidence.

The work of Dr. Lemon[3] by itself is inconclusive in this respect, since the effects observed might be due to the heat treatment or to oxidation, due to the presence of air, at the temperatures used. The results which have now been obtained using pure gases substantiate the hydrocarbon theory and at the same time facts have been revealed which show that, as it now stands it is incomplete.

In the case of hydrogen, for out-gassing temperatures below 600° C. the activity of the charcoal is not affected, which shows that activation below this temperature must be due entirely to oxidation. At 700° C. the activity is increased, showing that according to the hydrocarbon theory, the boiling points of some of the inactive hydrocarbons have been reached. When no further activation could be produced at this temperature, 800° C. was however, effective. At 900° C. de-activation was found to take place slowly, which indicated that the basic structure, or active carbon was being modified. The de-activation was very decided at 1000° C.

So far the evidence for the hydrocarbon hypothesis is excellent, but a most significant fact is that charcoals de-activated so far as the adsorption of nitrogen is concerned remain nearly as good for hydrogen as before treatment, regardless of what gases may have been in the charcoal during, or previous to the high temperature treatment. A sample of charcoal which, at liquid air temperature,

[1] Abstract of a paper presented at the Chicago meeting of the American Physical Society, November 28, 1919.

[2] J. Ind. and Eng. Chem., 1919, 11, 420–467. N. K. Chaney, Thirty-sixth General Meeting of the Amer. Electro-Chem. Society, Chicago.

[3] PHYS. REV., Vol. 14, No. 4, October, 1919.

will adsorb 2,000 c.c. (normal) of nitrogen, may be de-activated so as to adsorb 400 c.c. and still remain unchanged so far as hydrogen is concerned within 50 c.c. For example, a sample of 25.7 grams of a certain charcoal adsorbed 914 c.c. of hydrogen from an initial volume of 926 c.c. The same sample adsorbed all of the 926 c.c. of nitrogen, and on increasing the volume adsorbed 1,780 c.c. before it was saturated. A similar sample de-activated adsorbed 874 c.c. of hydrogen and only 406 c.c. of nitrogen. This results, then, in a charcoal which adsorbs hydrogen better than nitrogen and this furnishes a new material that may be of value in certain technical processes of gas purification.

The above fact also suggests that hydrogen adsorption must be, to some extent, a different thing from nitrogen adsorption, and it is suggested that, apart from surface condensation, the hydrogen may, at the same time, act chemically to form an easily dissociated hydrocarbon. Since this secondary action in the case of nitrogen would not be expected this would class hydrogen adsorption as quite different from nitrogen adsorption, as the facts seem to indicate. The work with pure nitrogen is not yet quite complete.

The method and apparatus used is similar to that described by Dr. Lemon,[3] to whom the author is indebted for advice and assistance in this work.

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THE ABSORPTION OF AIR BY CHARCOAL AT REDUCED PRESSURES NEAR LIQUID AIR TEMPERATURES.[1]

BY THOS. E. DOUBT, HARRY C. THOMPSON AND H. H. SHELDON.

IN the extraction of helium from natural gas and in other work of the War Department with charcoal it was deemed very desirable to find out how air was absorbed by charcoal under reduced pressure.

The rate of absorption as well as the amount per gram of charcoal was sought. The results are given both in the form of curves and in tables. The measurements were made at 1/5, 1/10 and 1/20 of an atmosphere for temperatures ranging from -160 to $-193°$ C.

AN APPARENT COMPRESSION BY ADSORPTION.[1]

BY W. D. HARKINS AND D. T. EWING.

WHEN liquids are taken up by a highly out-gassed charcoal, the volume of the liquid adsorbed increases considerably with an increase in the compressibility of the liquid. Unless this is a time effect, which has not been fully investigated, the most probable explanation is that the liquid is very highly compressed.

[1] Abstract of a paper presented at the Chicago meeting of the American Physical Society, November 28, 1919.

The Electric Field of a Rotating Magnetic Doublet.[1]

By W. F. G. Swann.

At the October, 1919, meeting of the American Physical Society, the writer presented a paper on "Unipolar Induction." One of the fundamental conclusions reached in that paper was that, to make the ordinary "Moving Magnetic Line Theory" agree with the Maxwell-Lorentz theory, it was necessary to treat independently the contributions from the different magnetic doublets which constitute a magnet, and to calculate the motion of the lines of force of each doublet as though they partook of the linear velocity of the doublet in its revolution about the center of rotation of the system as a whole, but not of the rotary velocity of the doublet about its own axis.

The paper now presented deals with the rotation of a doublet about an axis passing through its center and perpendicular to its own axis; for, while this problem is not fundamentally involved in the problem of unipolar induction, it is of interest on its own merits. It is shown that the moving line theory leads to the same result as that calculated from the Maxwell-Lorentz theory provided that, in applying it, we divide our doublet into two constituent poles, and calculate the velocity of the lines as though they partook of the linear velocities of the poles in their revolutions about the center of the doublet but not of their rotational velocities. In other words, we must treat the lines of force from each pole as though they were rigidly attached to a disc whose center is at the pole, and whose plane remains parallel to itself during the revolution of the two poles. The ordinary application of the moving line theory to this case would correspond to supposing that the lines from each pole were pinned down at the place where they passed through the center of the doublet, thus making them partake of the rotational velocities of the poles as well as of their translatory velocities in their orbits.

The Change of Molecular Kinetic Energy into Molecular Potential Energy—The Entropy Principle.[1]

By William D. Harkins and L. E. Roberts.

If a phase, a surface, or an interface, is considered as a *region*, the following statement will be found to express an important relation concerning the kinetics of the passage of molecules from one region to another in one component systems. In general, when molecules pass from one definite region to another, the average amount of energy per molecule which is changed from the kinetic into the potential form, increases with the temperature, and is often proportional to the absolute temperature—that is the molecules on the average transform a definite fraction of their kinetic energy of translation into potential energy for a definite regional change. Thus an average molecule in passing from the interior of a liquid into its surface uses 144 per cent. of the average

[1] Abstract of a paper presented at the Chicago meeting of the American Physical Society, November 28, 1919.

molecular kinetic energy, so in general only the more rapidly moving molecules are able to pass into the surface. The principle may also be stated in terms of entropy. Thus the entropy of the change is independent of the temperature, and in the case of the regional change from liquid to surface, is $2.96 \times 10^{-16} \frac{\text{ergs}}{\text{degrees}}$ per molecule, or $2.16k$, where k is the Boltzmann constant. For the fusion of organic liquids the entropy per molecule is about 9.2×10^{-16} ergs per degree, for the vaporization of a solid at the melting point, 20.7×10^{-16}, for the dissociation of solids, 22×10^{-16}, and for the vaporization of a liquid, 18.8×10^{-16} whenever the vapor has a concentration of 0.00507 mols per liter. While the relation here expressed seems to be independent of the nature of the molecules within certain limits, the condition which must be imposed in order that it may be exact seems to be somewhat similar to that in the case of Raoult's law, that is the substances which give the same value of any particular constant seem to have molecules which are somewhat alike, presumably with respect to their electromagnetic stray fields. This principle includes many empirical relations, such as those of Eotvos, Ramsay and Shields, of Trouton and Hildebrand, of Richards and Walden, of Forcrand, etc., and also shows under what conditions these empirical relations should hold.

Duration of the Light Emission from a Radiating Hydrogen Atom.[1]

By A. J. Dempster.

It is known that canal rays moving in a very high vacuum excite very little light, due to the rareness of the exciting impacts with gas molecules. In the experiments described in this paper canal rays were passed through a small hole directly from a discharge tube into a second tube with a very much higher vacuum. The object of the experiments was to make the pressure in the second chamber so low that the natural rate of dying out of the fast-moving luminous particles coming in from the discharge tube could be observed. The difference in pressure on the two sides of the hole was maintained by means of a mercury vapor pump which continually drove the gas from the second tube back into the discharge tube. By starting and stopping the mercury vapor pump the pressure in the second chamber could be changed from that of the discharge tube to a pressure very much lower without altering appreciably the pressure in the discharge tube itself.

With the same pressure on both sides of the hole the canal rays gave a luminous bundle extending the whole length of the second chamber. As the mercury vapor pump began to work the upper part of the bundle became fainter and, when the pump was in full operation, the second chamber was perfectly free from general gas luminosity, and the upper part of the canal ray bundle disappeared completely. The rays issuing from the hole in the cathode were still bright but died out gradually in a distance that could be readily observed.

[1] Abstract of a paper presented at the Chicago meeting of the American Physical Society, November 28, 1919.

With a discharge tube about 3 cm. in diameter, the bundle extended about 4 cm. beyond the hole before ceasing. The intensity of the rays could be varied from very faint to the maximum intensity by changing the current through the discharge tube without affecting the phenomena of dying out in 4 to 5 cm.; merely the total intensity being altered. In another tube 2.2 cm. in diameter where the discharge tube pressure was necessarily greater and the velocity of the rays less, the bundle was estimated to die out in 3–3.5 cm. The speed of the canal rays may be obtained from Doppler effect measurements, and for conditions similar to those in the first tube, the fastest rays have a speed of approximately 9×10^7 cm. per sec. The time required for the radiating particles to die out is therefore approximately 5×10^{-8} seconds. The light observed is practically entirely due to H_β.

The present value agrees in magnitude with an estimate made recently by Stark by a different method. For H_δ he obtains 4×10^{-7} secs. and states that the time for H_γ, H_β, H_α is less than this. He also observes that the higher members of the series require a longer time to emit their amount of radiation than the first members. This may be interpreted qualitatively on Bohr's atom model as indicating that an electron requires a longer time to return to the second orbit from a far distant ring than from one not so far out. Taking the value 5×10^{-8} there are approximately 3×10^{10} vibrations emitted during the return of the electron from the third ring to the second. If no other cause of inhomogeneity were present apart from natural damping interference should be obtained with path differences of 15 meters.

The author wishes to acknowledge his indebtedness to Mr. T. Takamine, who assisted in carrying out some of the experiments.

THE SPECTRO-PHOTO-ELECTRIC SENSITIVITY OF THALOFIDE.[1]

BY W. W. COBLENTZ.

CONTINUING the investigation of the spectro-photo-electric sensitivity of various substances, through the courtesy of Mr. T. W. Case, the writer has examined thalofide.[2]

This substance has a complex band of high photo-electrical sensitivity, with maxima in the region of 0.9 μ and 1 μ. At room temperature, it appears to be insensitive to radiation of wave-lengths greater than 1.3 μ.

The photo-electric response attains its maximum very quickly and unlike the selenium cell there is no great lag in recovery after exposure to light.

In view of its high sensitivity, an attempt should be made to use this device in measuring variable stars, etc. Used in connection with the potassium-hydride photo-electric cell, which is sensitive to the violet, valuable

[1] Abstract of a paper presented at the Chicago meeting of the American Physical Society, November 28, 1919.

[2] Thalofide is the name given to a laboratory preparation which was discovered by Mr. Case (Case Research Lab., Auburn, N. Y.) to be photoelectri cally sensitive.

information should result from simultaneous measurements with these two instruments.

WASHINGTON, D. C.,
November 11, 1919.

VIBRATIONAL FREQUENCIES OF THE HALOGEN ACID MOLECULES.[1]

BY W. F. COLBY.

A PAPER by Imes entitled "Measurements on the Near Infra-red Absorption of some Diatomic Gases" in the current number of the Astrophysical Journal shows that the absorption bands of three halogen acids in this region can be closely represented by the formula

$$\nu = \nu_{00} \pm \nu_r n - \alpha n^2,$$

where n indicates successive integers. In accordance with the Bjerrum postulate which ascribes these absorptions to a combination of rotation and interatomic vibration of the molecule, the present paper undertakes an investigation of a familiar molecular model in the hope of testing the above formula. The simplest model of the generally accepted type is slightly idealized into four equal electronic point charges. The two positive charges are associated with the masses of the H and Cl atoms respectively and held at a definite distance by the two negative charges (electrons) which are revolving in a circular orbit about the atomic axis halfway between the nuclei. The electrons have an angular momentum of $h/2\pi$. The whole system is capable of rotation about an axis through the centroid normal to the atomic axis with angular momenta which are integral multiples of $h/2\pi$.

The equilibrium equations are

$$n^2h^2/4\pi^2(2x)^3M + e^2/(2x)^2 = 2e^2x/(x^2 + y^2)^{\frac{3}{2}},$$
$$nh^2/4\pi^2y^3m \qquad + e^2/y^2 \quad = 2e^2y/(x^2 + y^2)^{\frac{3}{2}},$$

where $2x$ is the distance between the nuclei and y the radius of the electronic ring, m is the mass of the electron and M the reduced mass of the other (molecular) rotation.

An approximate solution for x gives

$$x = 2.917\ 10^{-9} + 1.23\ 10^{-12}n^2,$$

By this theory ν_r in Imes equation should equal $h/16\pi^2Mx^2$. The observed values of ν allow one therefore to calculate x. A comparison with the above equation shows that both constants are of the right order of magnitude and represent the observed values surprisingly closely.

One may solve similarly for the vibrational frequency and express the result by

$$\nu_0 = 1.4485\ 10^{14} - 4.63\ 10^{10}n^2,$$

[1] Abstract of a paper presented at the Chicago meeting of the American Physical Society, November 28, 1919.

which again agrees remarkably well with Imes formula

$$\nu_0 = \nu_{00} - \alpha n^2,$$

both in form and constants.

The above model gives results which agree numerically more closely with the experimental data for halogens of low atomic number which one might expect the point charge model to represent more accurately. The greater deviations for high number are doubtless due to the screening effect of the inner electrons about the atomic nucleus, a configuration which the above equations have not taken into account.

SYMMETRICAL SUBDIVISION OF ANODE GLOW IN HELIUM DISCHARGE TUBES.[1]

BY G. M. J. MACKAY.

THE anode glow produced by electrical discharge in helium at 2 cm. pressure may appear as a number of symmetrically arranged luminous dots, about 2 mm. in diameter. The most striking arrangement obtained is the three ring type, with one dot at the center of a regular pentagon, surrounded by eleven uniformly distributed about the circumference of the circular anode, 2.6 cm. in diameter.

RESEARCH LABORATORY,
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THE NUCLEI OF ATOMS AND THE NEW PERIODIC SYSTEM.[1]

BY W. D. HARKINS.

FORMER papers by the writer have proved that the abundance of complex atoms, and presumably the stability of the nuclei of the atoms, shows a periodicity such that the nuclei of the atoms of even and of odd nuclear charge fall into two classes. An even charge on the nucleus is accompanied by a very much greater abundance, and seemingly by a very much greater nuclear stability. The present paper continues the discussion of this periodicity, and gives some new relations concerning the composition and structure of the nuclei. Thus it is shown that the negative electrons in the nuclei are almost always associated in paris, not only in the helium nucleus, but also in the more complex nuclei. Hydrogen nuclei occur most frequently in groups of 4, less frequently in groups of 3, very seldom in groups of 2 except among the heavy atoms or in less abundant isope of neon, magnesium, silicon or chlorine, while in only one case, that of beryllium, is there a strong indication of a single hydrogen nucleus which is not associated in one of these sets. In the beryllium nucleus one hydrogen nucleus together with one negative electron serve the peculiar purpose of binding together two helium nuclei. From three to ten helium nuclei may alone unite to form a complex nucleus,

[1] Abstract of a paper presented at the Chicago meeting of the American Physical Society, November 28, 1919.

but when more than ten are included at least one extra helium nucleus is bound on by the inclusion of two negative electrons. Evidence of the existence of a meta-hydrogen is discussed, and it is also shown that *isomeric* as well as isotopic atoms, and also isomeric nuclei, exist. The composition of both light and heavy atoms is presented in the form of formulæ, together with formulæ for the nuclei of these atoms. The system proposed is based largely on, and is an extension of the ideas introduced in connection with radioactivity, especially by Rutherford, by Moseley, and by Soddy, and on the abundance and atomic weight relations of the atoms.

THE CONSTRUCTION OF THREE-ELEMENT POWER ELECTRON TUBES.

BY EARLE M. TERRY AND C. M. JANSKY, JR.

THE three-element electron tube has now been perfected to a stage where it is a very essential adjunct to every physical laboratory, as well as being of very great importance in its commercial applications. Unfortunately the patent situation is such that only one type of tube is procurable on the open market. The authors have devised a new form of electron tube, the construction of which is sufficiently simple so that it can be constructed in any laboratory which is ordinarily well equipped. Some of these tubes will be exhibited and their operational characteristics discussed and a number of applications described. The authors have also devised a new circuit for radio telephony and by use of these tubes have radio-phoned successfully from Madison to Great Lakes, one hundred miles, and from Madison to Chicago, one hundred and thirty miles. These tests will also be described.

EXPERIMENTS ON OSMOTIC-ELECTRIC ELECTROMOTIVE FORCES.[1]

BY A. P. CARMAN AND E. C. FRITTS, JR.

THE accepted theory of osmotic-electric currents (Strömungströme) and of electro-osmosis, is that due to Helmholtz, which assumes at the start an "electric double-layer" at the boundary between the liquid and the walls of the porous diaphragm or of the capillary tube. In more recent years, Perrin[2] and others have raised questions concerning the Helmholtz theory. Thus, "Perrin inclines to the opinion that the kind of material in the wall is not essential, that with pure water every material is neutral, and that the exceptions from this depend upon secondary influences, in particular on a certain degree of solubility of the material of the wall (for example of the glass)."[3] Perrin attempts to explain the electric double-layer at contact by the distribution of the ions of the ionized liquid at the boundary surface, the smaller ions forming a layer staying along the boundary wall. The following

[1] Abstract of a paper presented at the Chicago meeting of the American Physical Society, November 28, 1919.

[2] Journal d. chem. phys., 2, p. 601, 1904.

[3] Smoluchowski's statement of Perrin's position, Graetz's Handbuch d. Elek., II., 2, p. 407.

experiments have been made on the electromotive forces produced when water is forced through capillary tubes to test these theories. The electromotive forces were determined with a Wolff potentiometer and a standard cell. Some measurements were made with a quadrant electrometer but the potentiometer method was easier and found equally accurate. Pyrex glass, which has a negligible or zero solubility in water was used for tubes and also for the containing vessels. The "ordinary distilled" water was freshly distilled from rain water in a fine tin-lined steam-heated still. The "extra-distilled" water was redistilled in a quartz flask, heated on an electric furnace, and collected in a Pyrex flask. The Jena glass capillary was from a lot of special "apparatus" tubing imported a number of years ago by the department of physical chemistry for use in water conductivity experiments, etc. Capillary tubes of sulphur, rosin and sealing wax (imported "Bank of England") were prepared by drawing heated wires from rods of the material. The capillary tubes were of dimensions to obey Poiseuille's law. We find, as can be seen from the summary below, that the purer the water, and the less soluble the glass of the tube, the higher the electromotive forces produced. The effect of the material of the wall of the tubes is also shown in the tubes of sulphur, rosin and sealing wax. It is not yet evident how these results can be explained on Perrin's theory, particularly that with the purest distilled water with the least soluble glass, we get such very large electromotive forces. Further experiments are in progress with tubes of different materials and with different liquids, and also using the inverse phenomenon of electro-osmosis.

The following are the results of our experiments:

1. The results confirm the law as stated by Quincke and Helmholtz, that the osmotic electromotive force is strictly proportional to the pressure, provided the tube is long enough, and this for a considerable range of pressures (from 0 cm. to 42 cm. of Hg.). The temperature effect on the electromotive force in glass tubes is zero, between 10° C. and 80° C.

2. By using "extra-distilled" water in Pyrex glass tubes, we get osmotic electromotive force as high as 60 volts per atmosphere pressure, this for pressures up to 3.65 cm. of mercury. In a Pyrex tube with "ordinary distilled" water we get 8.4 volts per atmosphere. In a a special Jena "apparatus" glass tube with ordinary distilled water, we get an electromotive force of 2.4 volts per atmosphere, this up to pressures of 31 cm. of Hg.

3. With capillary tubes of sulphur, rosin, and sealing wax, using ordinary pure distilled water, the electromotive forces are smaller. The results were 1.17 volts per atmosphere for sulphur, 1.33 volts per atmosphere for rosin, 1.37 volts per atmosphere for sealing wax, using ordinary distilled water and with pressures up to 40 cm. of Hg.

Laboratory of Physics,
University of Illinois,
Urbana, Illinois,
November, 1919.

NEUTRAL MAGNETIZATION IN IRON.[1]

BY A. W. SMITH AND H. E. HAMMOND.

IN unsymmetrical hysteresis curve can be found in which the returning branch will pass through the zero point. It has lately been maintained that at this point the curve runs into, and is continued by, the normal magnetization curve. The present paper gives the results of careful measurements by the direct deflection method, and shows that the unsymmetrical hysteresis curve passes through the zero point with a greater slope than the magnetization curve, and continues above the latter throughout its length. The same characteristics are found in Swedish iron, cast iron, and cast steel, for hysteresis loops of various amplitudes. The results show that iron brought to the zero point along any hysteresis curve is in a definite state of magnetization, even though neutral, and in this condition it has a greater permeability than when it is demagnetized.

UNIVERSITY OF MICHIGAN.

THE RIGIDITY OF THE EARTH.[1]

BY A. A. MICHELSON AND HENRY G. GALE.

FROM November 20, 1916, to November 20, 1917, a continuous series of observations was made on the grounds of the Yerkes Observatory at Williams Bay, Wis., to determine the rigidity and viscosity of the earth. Tides were measured in an E-W and in a N-S pipe. The pipes, six inches in diameter, were buried six feet under ground, carefully levelled and half filled with water. The pipes ended in pits eight feet square and ten feet deep. The changes in water level were recorded by projecting horizontal interference fringes onto a narrow vertical slit in front of a moving picture film, which was drawn horizontally by clock work at the rate of about 2 cm. per hour. The light used was $\lambda 4358$ from an alternating current Cooper-Hewitt mercury lamp.

The observed tides were compared with tides computed for the same apparatus on the assumption of a perfectly rigid earth. The results are shown in the accompanying table, in which are given the amplitude of the observed tides in fringes, the ratio of these amplitudes to the amplitudes of the corresponding computed tides, and the acceleration in phase of the observed tides over the computed tides. R and $\Delta\phi$ were determined for each lunar month, and the table gives the average difference from the mean, following the mean values of R and $\Delta\phi$. Means were found by weighting the tides in proportion to their amplitudes, except that the N-S lunar diurnal tide was ignored, since the uncertainty here was very great, the amplitude being less than 0.5 fringe.

The experiment indicates that the rigidity of the earth is the same in the

[1] Abstract of a paper presented at the Chicago meeting of the American Physical Society, November 29, 1919.

N-S and E-W directions, and that $R = 0.690$ with a probable error of $\pm.004$. The lag of the earth tide behind the impressed forces is $\Delta\phi = 4°$.

TABLE.

	N-S.			E-W.		
	Amp.	R	$\Delta\phi$.	Amp.	R.	$\Delta\phi$.
Lunar semi-diurnal .	6.188	$0.6765 \pm .019$	$1°15' \pm 1°\ 2'$	9.375	$0.6915 \pm .007$	$5°54' \pm\ 56'$
Solar 12^h	3.150	$.716 \pm .041$	$5°35' \pm 3°12'$	4.429	$.681 \pm .018$	$5°30' \pm 1°28'$
Lunar diurnal . .	.408	$.584 \pm .200$	$7°46' \pm 15°$	3.799	$.698 \pm .023$	$38' \pm 3°28'$
Weighted means		0.6895	$2°41'$		0.6903	$4°34'$
Final values . . .	$R = 0.690 \pm .004$ $\Delta\phi = 4°$					

STROBOSCOPIC FORMULÆ USED BY POSKE, BY MICHELSON, AND BY REED RESPECTIVELY, FOR RATING TUNING FORKS, AS SPECIAL CASES OF THE MORE GENERAL STROBOSCOPIC EQUATION.[1]

BY L. E. DODD.

FOR rating tuning forks by the general method of coincidences particular formulæ for the particular cases have been employed. Thus Poske[2] used the relation

$$m = l \pm 1/s, \tag{1}$$

where m is the frequency of the test fork, l the frequency of illumination, and s the period of the image cycle, or optical beat. Again, apparatus by Michelson[3] required the formula

$$n = N \pm 1/s, \tag{2}$$

where n is absolute value of frequency of test fork, N the nearest integer to n, and s the number of flashes during the time of an optical beat. Further, Reed[4] employed with his experimental conditions the relation

$$Nt = n \pm c, \tag{3}$$

where N is frequency of test fork, t the period of the intermittent illumination, n an integer, and $c = 1/a$, where a is identical with s in (2).

Eqs. (1) and (2), while apparently of the same form, are two different relations. Moreover (1) has dimension of frequency, while (2) has no dimensions. Eqs. (2) and (3) are however similar. All three are special cases of the more general stroboscopic equation, which is given by Poske (*loc. cit.*) in the form

$$\mu n - \nu m = 1/2\tau, \tag{4}$$

[1] Abstract of a paper presented at the Chicago meeting of the American Physical Society, November 29, 1919.

[2] Pogg. Ann. d. Phys. u. Chem., Vol. 152, 1874, p. 448.

[3] Phil. Mag., Vol. 15, 1883, p. 84.

[4] PHYS. REV., Vol. 12, 1901, p. 279.

where μ/ν is a fraction at lowest terms expressing the nearest whole-numbered approximate ratio of the two fork frequencies, n and m, and τ is the half-period of the beat. Poske does not however refer to a relation between (4) and (1), when in fact the latter is a special case of the more general form. This general form was derived independently by the writer[1] from a study of the stroboscopic effect in the tonoscope of Seashore,[2] after the general expression for stroboscopic velocity had been derived,[3] which is

$$v_s = (A - n/m \cdot B)\, D_0, \tag{5}$$

where v_s is the stroboscopic velocity, A the frequency of dots in a given row on the rotating drum, n/m a fraction at lowest terms, B the frequency of illumination, and D_0 the distance between dots in a particular row on the drum. From (5) and an additional relation noted at that time, the form mentioned as being equivalent to (4), as given by Poske, was derived but with the notation

$$f = mA - nB, \tag{6}$$

where f is the frequency with which simple stroboscopic images pass the tonoscope scale, and the remaining symbols are the same as in (5). It is seen that the time interval between the transit of one image past the tonoscope scale and the transit of the image next following corresponds to the period of an optical beat in the apparatuses of the three investigators named.

Eqs. (1), (2) and (3) above are shown to be special cases of the general form (4) and (6).

NOTE ON THE THEORY OF LONGITUDINAL VIBRATIONS IN RODS HAVING INTERNAL LOSSES.[4]

BY W. G. CADY.

THE equations for vibrations of the type indicated in the title were derived in connection with an experimental investigation, an account of which will appear later. The fundamental equation is

$$\frac{\partial^2 \xi}{\partial t^2} = P \frac{\partial^2 \xi}{\partial x^2} + Q \frac{\partial^3 \xi}{\partial x^2 \partial t}, \tag{1}$$

in which P and Q are constants depending upon the material, P being Young's modulus divided by density, and Q proportional to the viscosity. Equation (1) is first solved for the case of free vibrations, assuming ξ to have the form

$$\xi = A\epsilon^{-ikx-(\alpha+i\omega)t},$$

exactly as in the well-known problem of plane waves in a viscous medium. General expressions are obtained for wave-length and logarithmic decrement, for any frequency, in terms of P and Q. Application is then made to a thin

[1] Iowa Acad. Sc. Proc., Vol. 25, 1918, p. 49.

[2] Sc. Am., May 13, 1916.

[3] Iowa Acad. Sc. Proc., Vol. 24, 1917, p. 221.

[4] Abstract of a paper presented at the Chicago meeting of the American Physical Society, November 29, 1919.

rod vibrating with both ends free, frequency and damping being derived for the fundamental and for any harmonic vibration.

In the treatment of forced vibrations, it is assumed that two simple-harmonic forces, of like amplitude but opposing phases, are applied at opposite ends of a rod of length l. The problem is, to find the amplitude and phase of the displacement at the ends of the rod. We write

$$\xi = A\epsilon^{-i\omega t},$$

in which A is a complex function of x. The terminal conditions are, that at the middle of the rod $\xi = 0$, while at the end,

$$E\frac{\partial \xi}{\partial x} = F_0\,\epsilon^{-i\omega t},$$

where E is Young's modulus and F_0 the maximum impressed pressure. A is found to be expressed thus:

$$A = \frac{F_0}{E\gamma \cosh \frac{\gamma l}{2}} \sin \gamma x,$$

where

$$\gamma^2 = \frac{\omega^2}{-P + i\omega Q},$$

ω being equal to $2\pi f$, and x the distance from the center of the rod.

The value assumed by A at the end of the rod is found, and from it the amplitude and phase of the displacement follow at once.

In applying these equations to actual cases, the numerical work is rather laborious. It would be a great advantage if the system could be treated as having only one degree of freedom, as this would greatly simplify the solution. A proof is furnished that, if the viscosity is small, the amplitude and phase relations in the neighborhood of resonance, on the assumption of one degree of freedom, are in very close agreement with those derived by the more general theory. Suitable values for the coefficients of inertia and stability must of course be assigned.

It is hoped that the expressions derived will afford a means for determining the coefficient of viscosity of a solid when in a state of rapid vibration.

Wesleyan University.

The Measurement of Very Short Time Intervals.[1]

By Paul E. Klopsteg.

A BRIEF review is given of the usual method of determining time intervals of the order of millionths of a second. Sources of error are discussed, and a simple modification of circuits proposed, which utilizes the advantages of partial deflection methods, thereby gaining the accuracy pertaining to such methods. The observations are easily made with the aid of a specially designed

[1] Abstract of a paper presented at the Chicago meeting of the American Physical Society, November 29, 1919.

double throw gang switch, which at the same time eliminates possible error from absorbed charge in the condenser. After the event being timed has occurred, the switch is thrown over, and a galvanometer throw which in most cases amounts to not over a centimeter or two is observed. The paper further gives a derivation of the working equation for computing the time interval from the observations. From the relations expressed in the equation, it follows that the attainable accuracy in the measurement should be practically that of a resistance, a resistance ratio, and a capacity value. Experimental results obtained with the aid of a Helmholtz pendulum are given in two tables. The probable error in the computed interval, based upon a single observation, does not exceed 0.15 per cent. in a total interval of 250 microseconds. The precision of measurement attained was such as to enable the determination of an overall temperature coefficient of the Helmholtz pendulum and its accessories. This coefficient, at a setting of the pendulum of 250 micro-seconds, amounted to approximately 1 microsecond per degree.

On the Effective Capacity and Resistance of a Condenser for High Frequency Currents.[1]

By F. C. Blake.

BY careful experiments on the free oscillations of a Lecher system as the capacity of the end condensers is changed by increasing the capacitive coupling, it is found that the capacity of an air condenser is independent of frequency. Lord Rayleigh's equations for the effective stiffness and the effective resistance of a circuit due to the mutual elastic reactions between two circuits each containing inductance, capacity and resistance are verified. In making this verification it is shown that the coefficient of elastic or capacitive coupling is the mutual elastance divided by the square root of the two self-elastances. The true relationships between the mutual and self-elastances and the mutual and self-capacities are pointed out. The effect of this upon vacuum tube construction is pointed out as well as the modern necessity for electrical and radio engineers thinking in terms of elastances instead of capacities at least when dealing with reacting circuits. It would seem that a beginning has been made toward the scientific development of electrostatic transformers.

On the Dielectric Constant of Kerosene and Water for High Frequency Currents.

By F. C. Blake and Charles Sheard.

BY means of the free oscillations of a Lecher system using a wave-length of 250 cm. the dielectric constants of kerosene and water were measured and found to be of the order of 1.7 and 4.4 respectively. These results are in agreement with those of F. Beaulard,[2] but differ widely from the results of

[1] Abstract of a paper presented at the Chicago meeting of the American Physical Society, November 29, 1919.

[2] Comptes Rendu, 141, 656, 1905; 144, 904, 1907; 146, 960, 1908.

most experimenters. It is believed that the latter results contain errors due to the conductivity of the water and the methods of measurement, especially due to the free ends of the Lecher wires used. It is also suggested that many experimenters when measuring the dielectric constant of water may have been measuring the wave length of some harmonic rather than the fundamental.

THE VISCOSITY-TEMPERATURE CURVES OF SIX VARIETIES OF OPTICAL GLASS.[1]

BY E. W. WASHBURN AND G. R. SHELTON.

THIS is a preliminary report of some experiments with an apparatus adapted to the study of the viscosity of any type of commercial glass. The method employed was that of Margules. A hollow porcelain cylinder was rotated in the molten glass contained in a co-axial cylindrical porcelain pot,

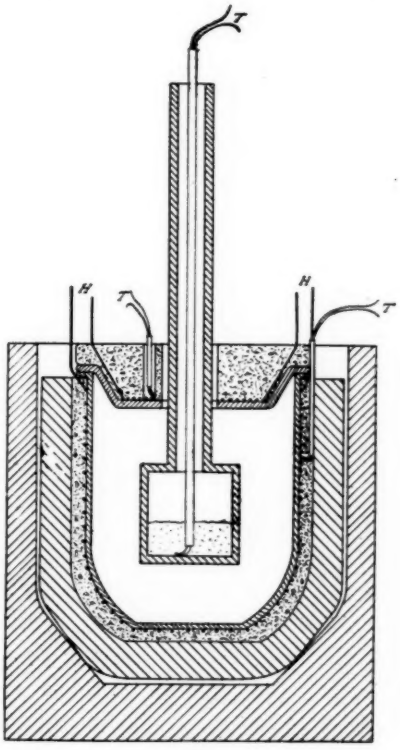

Fig. 1.

H, heating coils; *T*, thermocouples giving identical temperature readings.

both the pot and its cover being wound with platinum wire for the purpose of maintaining the glass at a definite temperature (Fig. 1). The force neces-

[1] Abstract of a paper presented at the Chicago meeting of the American Physical Society, November 29, 1919.

sary to drive the inner cylinder at a measured speed was determined, the viscosity of the liquid varying directly as the driving force and inversely as the speed. The apparatus was standardized with liquids of known viscosity.

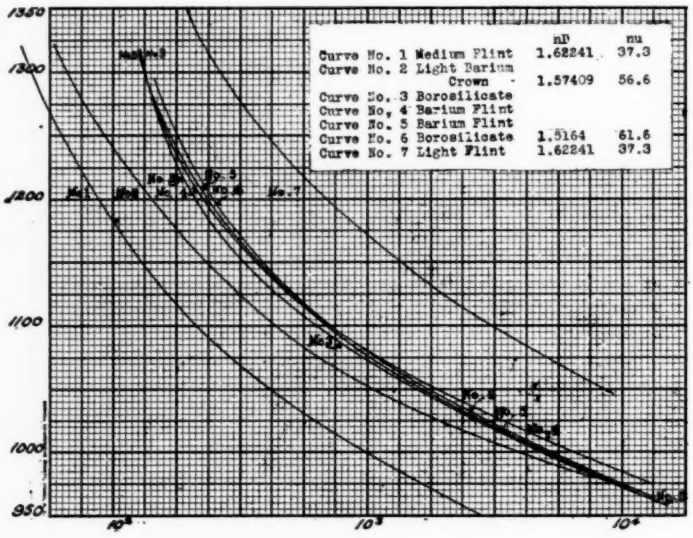

Fig. 2.

A thermocouple in the interior of the hollow cylinder and a second similar couple on the exterior surface of the pot served to measure the temperature of the melt. Preliminary results secured with six varieties of optical glass supplied by the Bureau of Standards are shown in the accompanying diagram (Fig. 2).

THE SPECTRAL DISTRIBUTION OF THE RADIANT ENERGY OF METALS.[1]

BY GROVER R. GREENSLADE.

FOR determining the spectral distribution of the radiant energy emitted by different metals, each specimen was rolled into a thin sheet and then folded in such a way as to form a V of small angle. The working temperatures could then be determined by focusing an optical pyrometer into the black body crevice of the V, while the polished outside surface of the metal was radiating to the analyzing apparatus.

This apparatus consisted of a reflecting spectrometer and a receiving bolometer. In order to minimize absorption the prism of the spectrometer was made of rock salt and the entire apparatus was mounted in a vacuum chamber. This chamber was equipped with windows for pyrometric observations, electrical leads for heating the specimen, and for connecting the bolometer with a galvanometer placed outside.

[1] Abstract of a paper presented at the Chicago meeting of the American Physical Society, November 28, 1919.

Energy curves for a number of different temperatures were taken for each of the following metals: gold, iron, nickel, cobalt, rhodium, iridium, molybdenum and tungsten. These curves, as presented, have been corrected for galvanometer drift, impurity of spectrum due to width of spectrometer slit, change of bolometer sensitivity due to slight pressure variations in the

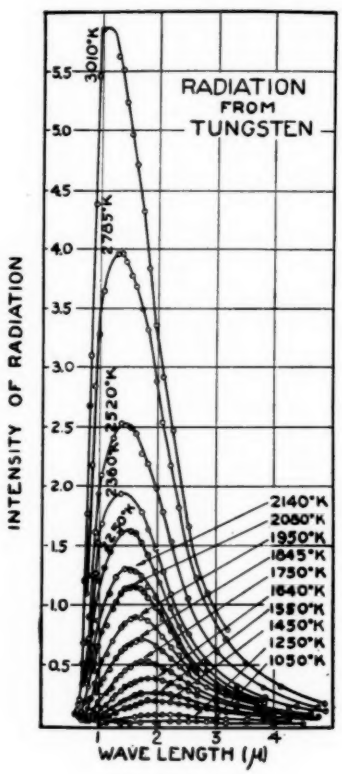

Fig. 1.

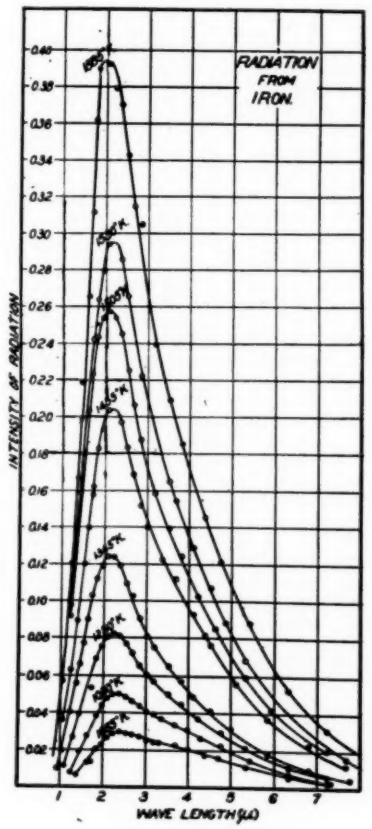

Fig. 2.

vacuum chamber, and for variations in spectral concentration due to the non-linear dispersion of rock salt. They have also been reduced to a common energy basis by comparison with an arbitrary standard source. This comparison standard was a small lamp placed inside the vacuum chamber and was entirely shielded except for a small aperture facing the bolometer. The opening and closing of this aperture was accomplished by means of an electromagnetic shutter.

It was found that the total radiated energy, as well as the form of the wave-length-energy curve varied with the purity of the metal. The extent of this variation may be seen from the following: one specimen of commercial nickel at 1353° K. had a total emission of 2.5 times that of electrolytic cobalt-free

nickel at the same temperature, and the energy for the wave-length of maximum emission was 3.0 times as great. This large difference was probably due to contamination of the surface by the ash contained in the impure specimen.

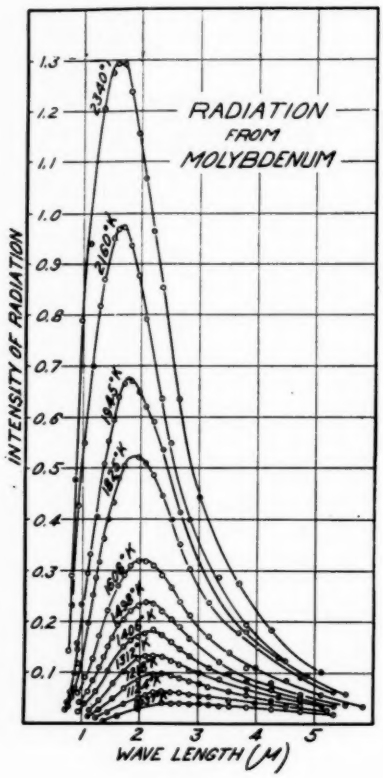

Fig. 3.

LABORATORY OF PHYSICS,
UNIVERSITY OF WISCONSIN,
November, 1919.

THE FINE-STRUCTURE OF THE NEAR INFRA-RED ABSORPTION BANDS OF THE GASES HCl, HBr, and HF.[1]

BY H. M. RANDALL AND E. S. IMES.

THE doublets which seemed characteristic of the near infra-red absorption spectra of a number of gases were supposedly explained by the combination principle of Rayleigh, viz: that an oscillator which emits and absorbs at a frequency ν_0 in the near infra-red due to its oscillations alone would, when rotating about an axis perpendicular to its line of vibration with a frequency ν_r corresponding to the far infra-red, emit and absorb at the additional fre-

[1] Abstract of a paper presented at the Chicago meeting of the American Physical Society, November 29, 1919.

quencies $\nu_0 + \nu_r$ and $\nu_0 - \nu_r$. With a maxwellian distribution of rotational velocities, the near infra-red band should consist of two broad absorption areas with maxima at $\nu_0 \pm \bar{\nu}_r$, where $\bar{\nu}_r$ is the most probable rotational frequency.

With higher resolution, the two broad absorption regions have been partially resolved into a number of narrow components whose explanation by the Rayleigh combination principle would require a number of distinct rotational frequencies. The quantum hypothesis would ascribe these to a series of stationary rotational states, in the far infra-red.

The partial resolution of these bands, which has been accomplished by the

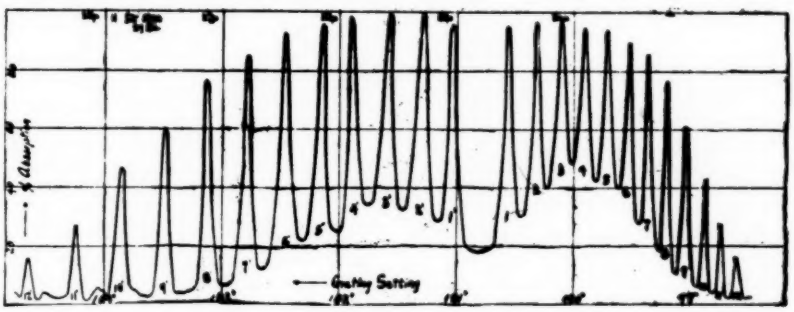

Fig. 1.

The HCl Band at 3.46n. Mapped with 7500-line grating. HCl at atmospheric pressure.

use of prism spectrometers, lacks both the necessary accuracy and completeness to justify the extended theoretical treatment necessary to test either the quantum ideas involved or to construct molecular models. Greatly increased resolution and accuracy has been obtained by using gratings in place of prisms as the dispersing agents. By focusing upon the slit of an infra-red grating spectrometer the spectrum produced by a prism spectrometer, using a salt prism of small refracting angle, the spectral region to be analyzed by the grating is too short for the overlapping of spectra, and it is possible to employ the full resolving power of a series of graded gratings with the result that in several instances the absorption curves show apparently complete resolution. The results are also more accurate, it being possible to determine the position of the narrow absorption bands with an accuracy of a few angstrom units.

The curve No. 1 shows the results obtained with the HCl band at 3.46 μ when the grating employed had 7,500 lines per inch, and the width of the spectrum falling upon the thermopile slit corresponding to 29AU. Each member of the earlier broad doublet is shown resolved into twelve narrow bands. The pairs $\nu_0 \pm \nu_{n,r}$ according to the Rayleigh principle, should be symmetrically grouped about the central position but the curve shows an unsymmetrical grouping. If the mid position of each pair represents the vibrational frequency, it is evident that, counting from the center of the band, the successive pairs have their centers located successively farther and farther toward the long wave-length end of the spectrum. This indicates that the vibrational frequency is a function of the rotational frequency and that the vibrational frequency is slowed down as the energy stored by rotation increases.

If the mid position of each pair be platted as ordinates against the number of the pair as abscissæ, curve No. 2 is obtained. The regularity of this curve is very suggestive of the accuracy of the results obtained and clearly shows the shift of the centers of each pair toward the long wave-length side of the absorption region. The equation of this curve $\nu_n = 2881.03 - .30\ N^2$ shows

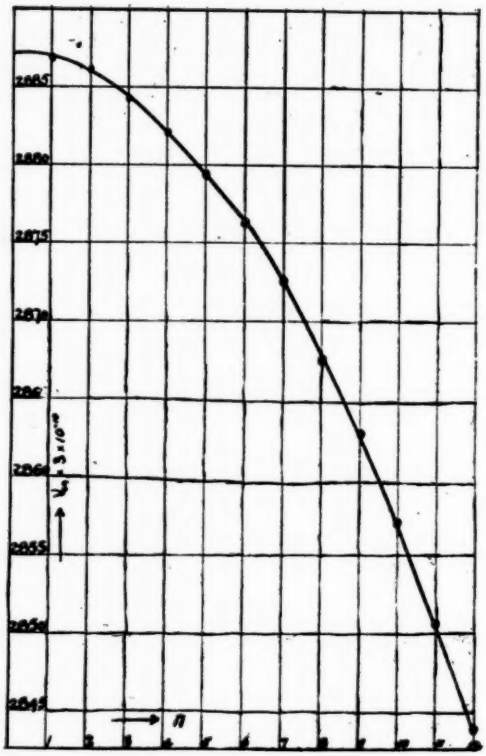

Fig. 2.

V_{0n}-n Curve for the HCl Band at 3.46 μ.

that the extrapolated center of the band, ν_0, is 2887.03. This is the vibrational frequency when uninfluenced by molecular rotation and corresponds to a wave-length of $\lambda_0 = 3.4637\ \mu$ as against $3.475\ \mu$ given by the original doublet maxima. Corresponding results in HBr and HF show $\lambda_0 = 3.9075\ \mu$ and $\lambda_0 = 2.5237\ \mu$ where the earlier result for HBr was $3.925\ \mu$.

If $\nu_{n,r}$ is the distance in terms of frequency of the individual band of each pair from their respective centers, then the relation

$$\nu_{n,r} = n \frac{h}{4\pi^2 I}$$

requires that $\nu_{n,r}/n$ should be a constant. The experimental results show in all three gases a slight diminution of this quality. This is most readily accounted for by assuming that I the moment of inertia of the molecule increases with the speed of rotation.

According to Kemble there should be a "harmonic" accompanying the band at 3.7 μ whose wave-length should be exactly one half that of the "fundamental." By using a grating having 20,000 lines per inch, the absorption curve shown in Fig. 3 was obtained. It shows the same general departures

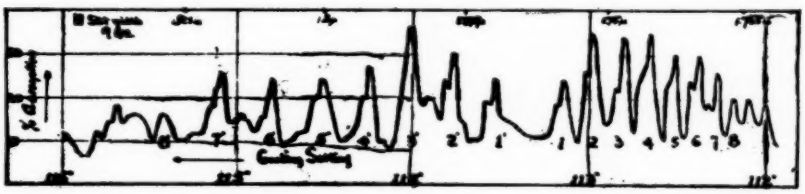

Fig. 3.

The HCl Band at 1.76 μ. Mapped with 20,000 line grating. HCl at atmospheric pressure.

from symmetry that the "fundamentals" do. The extrapolated center of this band lies at $\lambda_0 = 1.7646\,\mu$, distant .033 μ from $\frac{1}{2}$ of $\lambda_0 = 3.4637\,\mu$ toward the long wave-lengthside. The "harmonic" relationship is therefore not substantiated. The form of the curve indicates that there is still not complete resolution even with the dispersion furnished by 20,000-line grating. The moment of inertia and length of the molecule computed from the data obtained from the main maxima check with those obtained from the data of the fundamental.

The following table contains some molecular quantities computed from the data of this investigation. L is the distance separating the atoms.

Molecule.	$I \cdot 10^{40}$.	$L \cdot 10^{8}$.	$I \cdot 10^{40}$ (from Kinetic Theory).
HF.....	1.37	.14	
HCl.....	2.64	1.28	2.45
HBr.....	3.27	1.42	3.35

PHYSICAL LABORATORY,
UNIVERSITY OF MICHIGAN.

STUDY OF THE ENERGY OF POSSIBLE STANDARD OF SOUND.[1]

BY CHAS. T. KNIPP.

THE new source of sound, that was described and exhibited for the first time (by the writer) before the Pittsburgh meeting of the American Physical Society,[2] presents many interesting features. Recently the energy that is required to produce a given tone was quantitatively measured by employing a calometric method. This is possible since, in the case of this source, the sound is produced at the expenditure of heat energy. By placing the sounding tube in a calorimeter containing water, Fig. 1, it was found comparatively

[1] Abstract of a paper presented at the Chicago meeting of the American Physical Society, November 29, 1919.

[2] PHYS. REV., N. S., XII., No. 6, December, 1918.

easy to measure the heat energy absorbed by the water-bath, (*a*) when the tube is sounding, and (*b*) when the tube is stopped off. From these two quantities, together with the heat energy supplied in each case to the bath by the electric current, the energy required to maintain the tone emitted may be determined.

Let W_e = heat energy supplied to the calorimeter,
W_h = heat energy absorbed by bath,
W_s = energy absorbed in producing sound,
and W_o = other energy losses.
Then, we may write,

$$W_e = W_h + W_s + W_o.$$

The following table contains the data obtained on three different days.

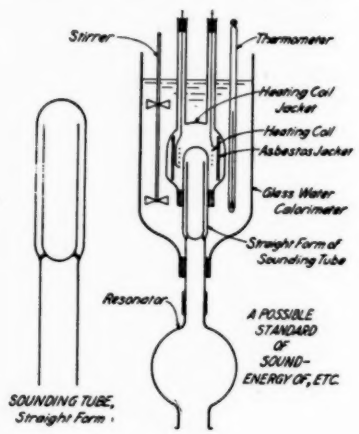

Fig. 1.

In the last column is recorded the per cent. of the total energy supplied that was used in maintaining the tone emitted by the sounding tube. This appears, under the conditions of the experiment, to be about two per cent.

	W_e Energy in Joules/Sec. Supplied.	W_h Energy in Joules/Sec. Absorbed.	W_s Ditto to Sound.	+ W_o Ditto to Other Losses.	W_o Net Other Losses.	W_s Net Sound.	Per Cent. of Total Energy Supplied to Sound.
Tube sounding.....	49.28	47.36	1.92				
Tube stopped off....	46.43	45.59			8.4	1.08	2.19
Tube sounding.....	47.91	45.73	2.18				
Tube stopped off....	47.94	46.67			1.27	.91	1.90
Tube sounding.....	48.82	46.39	2.43				
Tube stopped off....	48.09	46.54			1.55	.88	1.80

A sample of the straight form of tube, operated under different conditions as regards length of extensions and size of resonators, was exhibited.

LABORATORY OF PHYSICS,
UNIVERSITY OF ILLINOIS,
November, 1919.